Enantioselective Alkenylation via Nickel-Catalyzed Cross-Coupling with Organozirconium Reagents

Sha Lou and Gregory C. Fu*

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Supporting Information

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I. General Information

The following reagents were purchased and used without further purification: Cp_2ZrHCl (Strem; Aldrich), $NiCl_2$•glyme (Strem), 1,2-dimethyoxyethane (DME; anhydrous; Fluka), and THF (anhydrous; Aldrich). Ligands (–)-**1** and (+)-**1** were prepared according to a modified literature procedure[1] (for the cyclization of the amide-alcohol to the bis(oxazoline), 1,2-dichloroethane, rather than dichloromethane, was used, and the reaction was run at 70 °C for 24 h).[2] The α-bromoketones were prepared according to previously reported procedures.[3]

HPLC analyses were carried out on an Agilent 1100 Series system. Supercritical fluid chromatography (SFC) analyses were carried out on a Berger SFC MiniGram system. Daicel CHIRALCEL® columns or Daicel CHIRALPAK® columns (internal diameter 4.6 mm, column length 250 mm, particle size 5 μ) were used for both HPLC and SFC analysis.

All reactions were carried out in oven-dried glassware under an atmosphere of argon.

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(1) Ginotra, S. K.; Singh, V. K. *Org. Biomol. Chem.* **2007**, 5, 3932–3937.

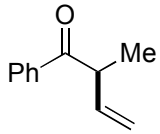
(2) Desimoni, G.; Faita, G.; Mella, M. *Tetrahedron* **1996**, *52*, 13649–13654.

(3) (a) Lundin, P. M.; Esquivias, J.; Fu, G. C. *Angew. Chem., Int. Ed.* **2009**, *48*, 154–156. (b) Lou, S.; Fu, G. C. *J Am. Chem. Soc.* **2010**, *132*, 1264–1266.

II. Asymmetric Cross-Couplings (Table 1–3)

General Procedure. Cp_2ZrHCl (Schwartz's reagent; 516 mg, 2.0 mmol; moisture-sensitive) was added to an oven-dried, 20-mL vial equipped with a magnetic stir bar, which was then closed with a septum-containing screw cap and purged with argon for 3 min. Anhydrous THF (2.0 mL) was added, and then the alkyne (2.0 mmol; over 2 min). The reaction mixture was stirred at room temperature for 60 min, at which time all of the white solid had been consumed and a homogeneous yellow solution was observed.

Into an oven-dried, 25-mL round-bottomed Schlenk flask equipped with a rubber septum and a magnetic stir bar under argon was added $NiCl_2$•glyme (6.6 mg, 0.030 mmol), ligand (–)-**1** (17.6 mg, 0.036 mmol), and anhydrous DME (8.0 mL). The pink catalyst solution was stirred for 10 min at room temperature, and then it was cooled in an isopropanol bath at 10 °C. The α-bromoketone (1.0 mmol) was added to the catalyst solution in one portion, and then the solution of the alkenylzirconium reagent (2.0 mmol) was added over 3 min. The reaction solution (yellow or orange) was stirred at 10 °C for 24 h, and then the reaction was quenched by the addition of methanol (2.0 mL). The solution was diluted with diethyl ether (20 mL) and washed with a saturated aqueous solution of sodium bicarbonate (15 mL). The organic layer was separated, and the aqueous layer was extracted with diethyl ether (15 mL×2). The organic fractions were combined, dried over anhydrous magnesium sulfate, and filtered through a bed of celite. The filtrate was concentrated by rotary evaporation, and the residue was purified by flash chromatography on silica gel to furnish the desired cross-coupling product.



(*S*)-2-Methyl-1-phenylbut-3-en-1-one (Table 1, entry 1). Cp_2ZrHCl (Schwartz's reagent; 516 mg, 2.0 mmol) was added to an oven-dried, 20-mL vial equipped with a magnetic stir bar, which was then closed with a septum-containing screw cap and purged with argon for 3 min. Anhydrous THF (5.0 mL) was added, and then acetylene gas was bubbled into the solution for 20 min, at which time all of the white solid had been consumed and a homogeneous yellow solution was observed. A portion of the solvent (~3.0 mL) was evaporated under reduced pressure (2.0 torr).[4]

The title compound was prepared according to the General Procedure with 2-bromo-1-phenylpropan-1-one (213 mg, 1.0 mmol). After purification by flash chromatography (eluted with 10→30% CH_2Cl_2 in hexanes), the title compound was isolated as a colorless oil (150 mg, 94% yield) with 90% ee (HPLC analysis of the product: Daicel CHIRALCEL OJ-H column;

(4) Erker, G.; Kropp, K.; Atwood, J. L.; Hunter, W. E. *Organometallics* **1983**, *2*, 1555–1561.

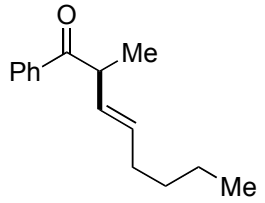
solvent system: 1.0% *i*-PrOH; 1.0 mL/min; retention times: 10.78 min (minor), 11.42 min (major)).

$[\alpha]^{22}_{D}$ = +40 (c = 1.0, $CHCl_3$).

The second run was performed with (+)-**1**. The product was isolated as a colorless oil (144 mg, 90% yield) with 90% ee.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.98 (d, *J* = 8.0 Hz, 2H), 7.56 (t, *J* = 8.0 Hz, 1H), 7.47 (t, *J* = 8.0 Hz, 2H), 6.04-5.97 (m, 1H), 5.20-5.13 (m, 2H), 4.18 (apparent quintet, *J* = 6.5 Hz, 1H), 1.34 (d, *J* = 6.5 Hz, 3H).

The spectral data are in agreement with literature values.[5]



(*S*,*E*)-2-Methyl-1-phenyloct-3-en-1-one (Table 1, entry 2). The title compound was prepared according to the General Procedure with 2-bromo-1-phenylpropan-1-one (213 mg, 1.0 mmol) and 1-hexyne (164 mg, 2.0 mmol). After purification by flash chromatography (eluted with 15→30% CH_2Cl_2 in hexanes), the title compound was isolated as a colorless oil (201 mg, 93% yield) with 92% ee (HPLC analysis of the product: Daicel CHIRALPAK OJ-H column; solvent system: 1.0% *i*-PrOH; 1.0 mL/min; retention times: 6.53 min (minor), 7.29 min (major)).

$[\alpha]^{21}_{D}$ = +82 (c = 1.0, $CHCl_3$).

The second run was performed with (+)-**1**. The product was isolated as a colorless oil (194 mg, 90% yield) with 92% ee.

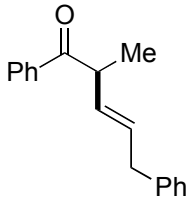
^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.99 (d, *J* = 8.0 Hz, 2H), 7.55 (t, *J* = 8.0 Hz, 1H), 7.45 (t, *J* = 8.0 Hz, 2H), 5.59-5.56 (m, 2H), 4.12 (apparent quintet, *J* = 7.0 Hz, 1H), 2.01-1.97 (m, 2H), 1.30 (d, *J* = 7.0 Hz, 3H), 1.32-1.22 (m, 4H), 0.85 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 201.9, 136.6, 133.2, 132.9, 129.8, 128.7 (2C), 128.6 (2C), 44.7, 32.4, 31.4, 22.2, 17.7, 14.0.

IR (film) 2929, 1685, 1596, 1448, 1215, 973, 704 cm^{-1}.

LRMS (ESI) calcd for $C_{15}H_{21}O$ (M+H) 217.2, found 217.2.

(5) Kachinsky, J. L. C.; Salomon, R. G. *J. Org. Chem.* **1986**, *51*, 1393–1401.



(*S*,*E*)-2-Methyl-1,5-diphenylpent-3-en-1-one (Table 1, entry 3). The title compound was prepared according to the General Procedure with 2-bromo-1-phenylpropan-1-one (213 mg, 1.0 mmol) and 3-phenyl-1-propyne (232 mg, 2.0 mmol). After purification by flash chromatography (eluted with 50% toluene in hexanes), the title compound was isolated as a colorless oil (230 mg, 92% yield) with 93% ee (SFC analysis of the product: Daicel CHIRALPAK AD-H column; solvent system: 5.0% MeOH; 3.0 mL/min; retention times: 4.15 min (major), 4.49 min (minor)).

$[\alpha]^{22}_{D}$ = +96 (c = 1.0, $CHCl_3$).

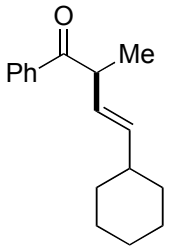
The second run was performed with (+)-**1**. The product was isolated as a colorless oil (225 mg, 90% yield) with 92% ee.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.90 (d, *J* = 8.0 Hz, 2H), 7.56 (t, *J* = 8.0 Hz, 1H), 7.46 (t, *J* = 2.0 Hz, 2H), 7.24 (t, *J* = 8.0 Hz, 2H), 7.19 (t, *J* = 8.0 Hz, 1H), 7.10 (d, *J* = 8.0 Hz, 2H), 5.78-5.68 (m, 2H), 4.17 (apparent quintet, *J* = 6.5 Hz, 1H), 3.33 (d, *J* = 7.0 Hz, 2H), 1.33 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 201.8, 136.6, 133.1, 131.55, 131.51, 128.78 (4C), 128.74 (2C), 128.63, 128.56, 128.2, 126.3, 44.8, 39.2, 17.7.

IR (film) 3026, 2930, 1684, 1597, 1494, 1451, 1212, 973, 699 cm^{-1}.

LRMS (EI) calcd for $C_{18}H_{19}O$ (M+H) 251.1, found 251.1.



(*S*,*E*)-4-Cyclohexyl-2-methyl-1-phenylbut-3-en-1-one (Table 1, entry 4). The title compound was prepared according to the General Procedure with 2-bromo-1-phenylpropan-1-one (213 mg, 1.0 mmol) and cyclohexylacetylene (216 mg, 2.0 mmol). After purification by flash chromatography (eluted with 15→30% CH_2Cl_2 in hexanes), the title compound was isolated as a colorless oil (179 mg, 74% yield) with 80% ee (SFC analysis of the product: Daicel CHIRALPAK AD-H column; solvent system: 2.5% MeOH; 3.0 mL/min; retention times: 4.85 min (major), 5.51 min (minor)).

$[\alpha]^{21}_{D}$ = +44 (c = 1.0, $CHCl_3$).

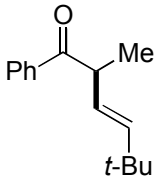
The second run was performed with (+)-**1**. The product was isolated as a colorless oil (182 mg, 75% yield) with 81% ee.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.96 (d, *J* = 8.0 Hz, 2H), 7.52 (t, *J* = 8.0 Hz, 1H), 7.43 (t, *J* = 8.0 Hz, 2H), 5.53-5.45 (m, 2H), 4.10-4.04 (m, 1H), 1.91-1.86 (m, 1H), 1.68-1.56 (m, 5H), 1.27 (d, *J* = 7.0 Hz, 3H), 1.26-0.94 (m, 5H).

^{13}C NMR ($CDCl_3$, 75 MHz) δ 202.1, 139.1, 136.7, 133.0, 128.8 (2C), 128.7 (2C), 127.6, 45.0, 40.9, 33.00, 32.97, 26.34, 26.20, 26.17, 17.9.

IR (film) 2924, 1686, 1596, 1448, 1345, 1220, 974, 706 cm^{-1}.

LRMS (ESI) calcd for $C_{17}H_{23}O$ (M+H) 243.2, found 243.2.



(*S*,*E*)-2,5,5-Trimethyl-1-phenylhex-3-en-1-one (Table 1, entry 5). The title compound was prepared according to the General Procedure with $NiCl_2$•glyme (21.9 mg, 0.10 mmol), ligand (–)-**1** (58.4 mg, 0.12 mmol), 2-bromo-1-phenylpropan-1-one (213 mg, 1.0 mmol), and *t*-butylacetylene (164 mg, 2.0 mmol). After purification by flash chromatography (eluted with 30% CH_2Cl_2 in hexanes), the title compound was isolated as a colorless oil (190 mg, 88% yield) with 84% ee (HPLC analysis of the product: Daicel CHIRALPAK IA-H column; solvent system: 0.5% *i*-PrOH; 1.0 mL/min; retention times: 7.51 min (major), 7.86 min (minor)).

$[\alpha]^{22}_D$ = +25 (c = 1.0, $CHCl_3$).

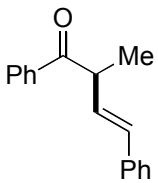
The second run was performed with (+)-**1**. The product was isolated as a colorless oil (183 mg, 84% yield) with 84% ee.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.97 (d, *J* = 8.0 Hz, 2H), 7.53 (t, *J* = 8.0 Hz, 1H), 7.45 (t, *J* = 8.0 Hz, 2H), 5.61 (d, *J* = 16.0 Hz, 1H), 5.45 (dd, *J* = 16.0, 8.0 Hz, 1H), 4.08 (apparent quintet, *J* = 7.0 Hz, 1H), 1.29 (d, *J* = 7.0 Hz, 3H), 0.95 (s, 9H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 202.3, 144.1, 136.8, 133.0, 128.8 (2C), 128.7 (2C), 125.0, 45.0, 33.3, 29.6 (3C), 18.1.

IR (film) 2960, 1685, 1448, 1363, 1215, 976, 704 cm^{-1}.

LRMS (EI) calcd for $C_{15}H_{21}O$ (M+H) 217.2, found 217.2.



(*S*,*E*)-2-Methyl-1,4-diphenylbut-3-en-1-one (Table 1, entry 6). The title compound was prepared according to the General Procedure with 2-bromo-1-phenylpropan-1-one (213 mg, 1.0

mmol) and phenylacetylene (204 mg, 2.0 mmol). After purification by flash chromatography (eluted with 20→50% CH_2Cl_2 in hexanes), the title compound was isolated as a colorless oil (208 mg, 88% yield) with 90% ee (SFC analysis of the product: Daicel CHIRALPAK AD-H column; solvent system: 5.0% MeOH; 3.0 mL/min; retention times: 6.61 min (major), 7.50 min (minor)).

$[\alpha]^{22}_D$ = +82 (c = 1.1, $CHCl_3$).

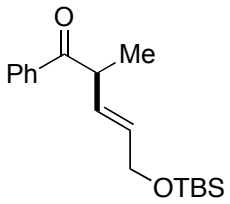
The second run was performed with (+)-**1**. The product was isolated as a colorless oil (212 mg, 90% yield) with 91% ee.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.02 (d, *J* = 7.0 Hz, 2H), 7.56 (t, *J* = 7.0 Hz, 1H), 7.47 (t, *J* = 7.0 Hz, 2H), 7.34 (d, *J* = 7.0 Hz, 2H), 7.28 (t, *J* = 7.0 Hz, 2H), 7.22 (t, *J* = 7.0 Hz, 1H), 6.52 (d, *J* = 16.0 Hz, 1H), 6.36 (dd, *J* = 16.0, 8.0 Hz, 1H), 4.33 (apparent quintet, *J* = 7.0 Hz, 1H), 1.43 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 201.3, 137.1, 133.4, 131.8, 129.9, 128.9 (4C), 128.8 (2C), 128.7 (2C), 127.7, 126.5, 45.1, 17.9.

IR (film) 2974, 1683, 1597, 1494, 1448, 1203, 972, 704 cm^{-1}.

LRMS (ESI) calcd for $C_{17}H_{17}O$ (M+H) 237.1, found 237.1.



(*S*,*E*)-5-(*tert*-Butyldimethylsilyloxy)-2-methyl-1-phenylpent-3-en-1-one (Table 1, entry 7). The title compound was prepared according to the General Procedure with 2-bromo-1-phenylpropan-1-one (213 mg, 1.0 mmol) and *tert*-butyldimethyl(prop-2-yn-1-yloxy)silane (341 mg, 2.0 mmol). After purification by flash chromatography (eluted with 15→30% CH_2Cl_2 in hexanes), the title compound was isolated as a colorless oil (248 mg, 82% yield) with 89% ee (SFC analysis of the product: Daicel CHIRALCEL OJ-H column; solvent system: 2.5% EtOH; 3.0 mL/min; retention times: 1.81 min (minor), 2.11 min (major)).

The second run was performed with (+)-**1**. The product was isolated as a colorless oil (240 mg, 79% yield) with 91% ee.

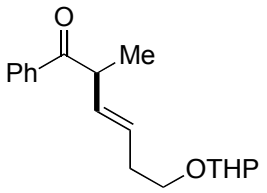
$[\alpha]^{22}_D$ = +22 (c = 1.0, $CHCl_3$).

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.95 (d, *J* = 8.0 Hz, 2H), 7.53 (t, *J* = 8.0 Hz, 1H), 7.43 (t, *J* = 8.0 Hz, 2H), 5.83-5.78 (m, 1H), 5.68-5.63 (m, 1H), 4.15 (apparent quintet, *J* = 6.5 Hz, 1H), 4.11 (d, *J* = 5.0 Hz, 2H), 1.30 (d, *J* = 6.5 Hz, 3H), 0.84 (s, 9H), –0.01 (s, 3H), -0.02 (s, 3H).

^{13}C NMR ($CDCl_3$, 75 MHz) δ 201.4, 136.5, 133.1, 131.6, 130.1, 128.7 (4C), 63.7, 44.2, 26.1 (3C), 18.5, 17.3, –5.03, –5.05.

IR (film) 2930, 2856, 1687, 1597, 1448, 1373, 1255, 1117, 1077, 974, 837, 777, 703 cm^{-1}.

LRMS (ESI) calcd for $C_{18}H_{29}O_2Si$ (M+H) 305.2, found 305.2.



(2*S*,*E*)-2-Methyl-1-phenyl-6-(tetrahydro-2*H*-pyran-2-yloxy)hex-3-en-1-one (Table 1, entry 8). The title compound was prepared according to the General Procedure with 2-bromo-1-phenylpropan-1-one (213 mg, 1.0 mmol) and 2-(but-3-yn-1-yloxy)tetrahydro-2*H*-pyran (308 mg, 2.0 mmol). After purification by flash chromatography (eluted with 2→10% MeOH in CH_2Cl_2), the title compound was isolated as a colorless oil (220 mg, 77% yield) with 95% ee (HPLC analysis of the product: Daicel CHIRALCEL AD-H column; solvent system: 10.0% *i*-PrOH; 1.0 mL/min; retention times: 14.4 min (minor), 15.4 min (major).

The second run was performed with (+)-**1**. The product was isolated as a colorless oil (215 mg, 75% yield) with 95% ee.

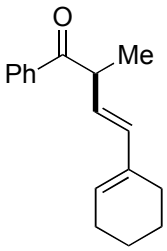
$[\alpha]^{22}_D$ = +52 (c = 1.2, $CHCl_3$).

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.96 (d, *J* = 8.0 Hz, 2H), 7.53 (t, *J* = 8.0 Hz, 1H), 7.43 (t, *J* = 8.0 Hz, 2H), 5.65-5.58 (m, 2H), 4.52 (dd, *J* = 4.0, 2.0 Hz, 1H), 4.11 (apparent quintet, *J* = 7.0 Hz, 1H), 3.77 (t, *J* = 10.0 Hz, 1H), 3.70-3.66 (m, 1H), 3.44-3.40 (m, 1H), 3.38-3.33 (m, 1H), 2.29 (apparent q, *J* = 6.0 Hz, 2H), 1.76-1.72 (m, 1H), 1.66-1.61 (m, 1H), 1.55-1.45 (m, 4H), 1.28 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR ($CDCl_3$, 75 MHz) δ 201.5, 136.5, 133.0, 131.9, 128.7 (3C), 128.6 (2C), 98.7, 66.9, 62.3, 44.7, 33.2, 30.8, 25.6, 19.6, 17.7.

IR (film) 2938, 2856, 1685, 1596, 1448, 1351, 1200, 1119, 1076, 1030, 970, 869, 705 cm^{-1}.

LRMS (ESI) calcd for $C_{18}H_{25}O_3$ (M+H) 289.2, found 289.2.



(*S*,*E*)-4-(Cyclohex-1-en-1-yl)-2-methyl-1-phenylbut-3-en-1-one (Table 1, entry 9). The title compound was prepared according to the General Procedure with 2-bromo-1-phenylpropan-1-one (213 mg, 1.0 mmol) and 1-ethynylcyclohex-1-ene (212 mg, 2.0 mmol). After purification by flash chromatography (eluted with 20→50% CH_2Cl_2 in hexanes), the title compound was isolated as a colorless oil (195 mg, 81% yield) with 93% ee (SFC analysis of the product: Daicel

CHIRALPAK AD-H column; solvent system: 2.5% MeOH; 3.0 mL/min; retention times: 8.23 min (major), 8.99 min (minor).

$[\alpha]^{22}_{D}$ = +30 (c = 1.0, $CHCl_3$).

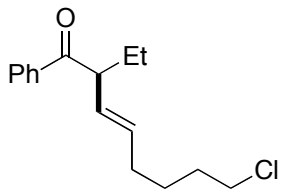
The second run was performed with (+)-**1**. The product was isolated as a colorless oil (197 mg, 82% yield) with 92% ee.

^{1}H NMR ($CDCl_3$) δ 7.97 (d, *J*=8.0 Hz, 2H), 7.52 (t, *J* = 8.0 Hz, 1H), 7.43 (t, *J* = 8.0 Hz, 2H), 6.14 (d, *J* = 16.0 Hz, 1H), 5.67 (t, *J* = 4.0 Hz, 1H), 5.62 (dd, *J* = 16.0, 8.0 Hz, 1H), 4.17 (apparent quintet, *J* = 7.0 Hz, 1H), 2.09-2.05 (m, 4H), 1.63-1.58 (m, 2H), 1.56-1.53 (m, 2H), 1.31 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR ($CDCl_3$, 75 MHz) δ 210.7, 136.6, 135.5, 133.1, 129.6, 128.8, 128.7 (4C), 125.7, 44.9, 26.0, 24.6, 22.6, 22.5, 18.0 cm^{-1}.

IR (film) 2928, 1682, 1596, 1448, 1341, 1237, 1202, 972, 707 cm^{-1}.

LRMS (ESI) calcd for $C_{17}H_{21}O$ (M+H) 241.2, found 241.2.



(*S*,*E*)-8-Chloro-2-ethyl-1-phenyloct-3-en-1-one (Table 2, entry 1). The title compound was prepared according to the General Procedure with 2-bromo-1-phenylbutan-1-one (227 mg, 1.0 mmol) and 6-chloro-1-hexyne (233 mg, 2.0 mmol). After purification by flash chromatography (eluted with 10→30% CH_2Cl_2 in hexanes), the title compound was isolated as a colorless oil (222 mg, 84% yield) with 91% ee (SFC analysis of the product: Daicel CHIRALPAK AD-H column; solvent system: 5.0% MeOH; 3.0 mL/min; retention times: 3.41 min (major), 3.85 min (minor)).

$[\alpha]^{22}_{D}$ = +37 (c = 1.0, $CHCl_3$).

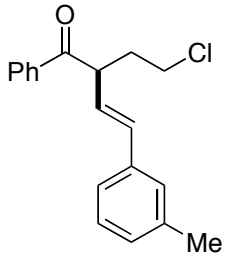
The second run was performed with (+)-**1**. The product was isolated as a colorless oil (214 mg, 81% yield) with 92% ee.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.96 (d, *J* = 7.0 Hz, 2H), 7.53 (t, *J* = 7.0 Hz, 1H), 7.45 (t, *J* = 7.0 Hz, 2H), 5.57-5.47 (m, 2H), 3.88 (apparent quintet, *J* = 6.5 Hz, 1H), 3.47 (t, *J* = 6.5 Hz, 2H), 2.03 (q, *J* = 6.0 Hz, 2H), 1.91-1.85 (m, 1H), 1.70-1.66 (m, 2H), 1.63-1.57 (m, 1H), 1.50-1.44 (m, 2H), 0.91 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR ($CDCl_3$, 75 MHz) δ 201.7, 137.1, 133.4, 133.0, 129.4, 128.7 (2C), 128.6 (2C), 52.5, 45.1, 32.0, 31.9, 26.5, 25.7, 12.1.

IR (film) 2934, 1683, 1597, 1580, 1448, 1274, 1210, 972, 704 cm^{-1}.

LRMS (ESI) calcd for $C_{16}H_{22}ClO$ (M+H) 265.1, found 265.1.



(*S*,*E*)-2-(2-Chloroethyl)-1-phenyl-4-(*m*-tolyl)but-3-en-1-one (Table 2, entry 2). The title compound was prepared according to the General Procedure with 2-bromo-4-chloro-1-phenylbutan-1-one (262 mg, 1.0 mmol) and *m*-tolylacetylene (232 mg, 2.0 mmol). After purification by flash chromatography (eluted with 10→30% CH_2Cl_2 in hexanes), the title compound was isolated as a colorless oil (281 mg, 94% yield) with 80% ee (HPLC analysis of the product: Daicel CHIRALPAK OD-H column; solvent system: 5.0% *i*-PrOH in hexanes; 1.0 mL/min; retention times: 5.82 min (major), 6.74 min (minor)).

$[\alpha]^{22}_D$ = +48 (c = 1.0, $CHCl_3$).

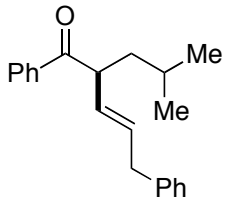
The second run was performed with (+)-**1**. The product was isolated as a colorless oil (284 mg, 95% yield) with 80% ee.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.04 (d, *J* = 8.0 Hz, 2H), 7.55 (t, *J* = 8.0 Hz, 1H), 7.45 (t, *J* = 8.0 Hz, 2H), 7.18-7.12 (m, 3H), 7.03 (d, *J* = 6.0 Hz, 1H), 6.58 (d, *J* = 16.0 Hz, 1H), 6.17 (dd, *J* = 16.0, 9.0 Hz, 1H), 4.56 (q, *J* = 6.0 Hz, 1H), 3.63 (t, *J* = 6.0 Hz, 2H), 2.42-2.35 (m, 1H), 2.30 (s, 3H), 2.18-2.11 (m, 1H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 199.9, 138.4, 136.5, 136.4, 134.5, 133.5, 128.90 (2C), 128.86, 128.84 (2C), 128.7, 127.2, 126.5, 123.7, 47.7, 43.1, 34.5, 21.5.

IR (film) 2958, 1682, 1597, 1581, 1447, 1290, 1258, 1204, 970, 775, 707 cm^{-1}.

LRMS (ESI) calcd for $C_{19}H_{20}ClO$ (M+H) 299.1, found 299.1.



(*S*,*E*)-2-Isobutyl-1,5-diphenylpent-3-en-1-one (Table 2, entry 3). The title compound was prepared according to the General Procedure with 2-bromo-4-methyl-1-phenylpentan-1-one (255 mg, 1.0 mmol) and 3-phenyl-1-propyne (232 mg, 2.0 mmol). After purification by flash chromatography (eluted with 10→30% CH_2Cl_2 in hexanes), the title compound was isolated as a colorless oil (225 mg, 77% yield) with 80% ee (SFC analysis of the product: Daicel CHIRALPAK AD-H column; solvent system: 2.5% MeOH; 3.0 mL/min; retention times: 4.89 min (major), 5.11 min (minor)).

$[\alpha]^{22}_D$ = +36 (c = 1.0, $CHCl_3$).

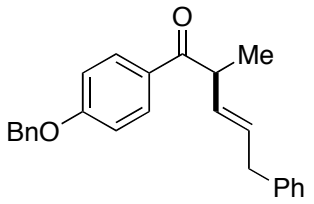
The second run was performed with (+)-**1**. The product was isolated as a colorless oil (248 mg, 85% yield) with 84% ee.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.95 (d, *J* = 8.0 Hz, 2H), 7.53 (t, *J* = 8.0 Hz, 1H), 7.44 (t, *J* = 8.0 Hz, 2H), 7.22 (t, *J* = 7.5 Hz, 2H), 7.16 (t, *J* = 7.5 Hz, 1H), 7.06 (d, *J* = 7.5 Hz, 2H), 5.73-5.67 (m, 1H), 5.60-5.54 (dd, *J* = 15.0, 8.5 Hz, 1H), 4.13 (q, *J* = 8.5 Hz, 1H), 3.32 (d, *J* = 7.0 Hz, 2H), 1.74-1.68 (m, 1H), 1.64-1.59 (m, 1H), 1.52-1.48 (m, 1H), 0.89 (d, *J* = 6.5 Hz, 3H), 0.88 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 201.6, 140.3, 133.1, 132.3, 130.7, 128.8 (2C), 128.64 (4C), 128.56 (2C), 128.3, 126.2, 48.8, 41.4, 39.2, 25.8, 23.3, 22.4.

IR (film) 2955, 1684, 1596, 1495, 1447, 1206, 972, 740, 698 cm^{-1}.

LRMS (ESI) calcd for $C_{21}H_{25}O$ (M+H) 293.2, found 293.2.



(*S*,*E*)-1-(4-(Benzyloxy)phenyl)-2-methyl-5-phenylpent-3-en-1-one (Table 2, entry 4). The title compound was prepared according to the General Procedure with 1-(4-(benzyloxy)phenyl)-2-bromopropan-1-one (319 mg, 1.0 mmol) and 3-phenyl-1-propyne (232 mg, 2.0 mmol). After purification by flash chromatography (eluted with 30→70% CH_2Cl_2 in hexanes), the title compound was isolated as a colorless oil (315 mg, 88% yield) with 94% ee (SFC analysis of the product: Daicel CHIRALPAK AD-H column; solvent system: 15% MeOH; 3.0 mL/min; retention times: 10.6 min (major), 12.4 min (minor)).

$[\alpha]^{21}_D$ = +28 (c = 1.0, $CHCl_3$).

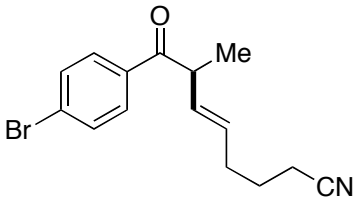
The second run was performed with (+)-**1**. The product was isolated as a colorless oil (321 mg, 90% yield) with 95% ee.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.98 (d, *J* = 8.5 Hz, 2H), 7.45-7.41 (m, 4H), 7.36 (t, *J* = 8.5 Hz, 1H), 7.26 (t, *J* = 7.5 Hz, 2H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.12 (d, *J* = 7.0 Hz, 2H), 7.01 (d, *J* = 8.5 Hz, 2H), 5.73-5.69 (m, 2H), 5.14 (s, 2H), 4.12 (apparent quintet, *J* = 7.0 Hz, 1H), 3.35 (d, *J* = 5.5 Hz, 2H), 1.32 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 200.2, 162.6, 140.3, 136.3, 131.9, 131.5, 131.1, 131.0 (2C), 128.9 (2C), 128.6 (2C), 128.5 (2C), 128.4, 127.6 (2C), 126.2, 114.7 (2C), 70.2, 44.3, 39.1, 17.8.

IR (film) 2930, 1675, 1599, 1507, 1453, 1373, 1251, 1169, 973, 842, 736, 697 cm^{-1}.

LRMS (ESI) calcd for $C_{25}H_{25}O_2$ (M+H) 357.2, found 357.2.



(*S*,*E*)-8-(4-Bromophenyl)-7-methyl-8-oxooct-5-enenitrile (Table 2, entry 5). The title compound was prepared according to the General Procedure with 2-bromo-1-(4-bromophenyl)propan-1-one (292 mg, 1.0 mmol) and 5-cyano-1-pentyne (186 mg, 2.0 mmol). After purification by flash chromatography (eluted with 30→70% CH_2Cl_2 in hexanes), the title compound was isolated as a colorless oil (220 mg, 72% yield) with 90% ee (HPLC analysis of the product: Daicel CHIRALCEL OD-H column; solvent system: 5% *i*-PrOH; 1.0 mL/min; retention times: 12.1 min (major), 12.8 min (minor)).

$[\alpha]^{21}_D$ = +3.3 (c = 1.0, $CHCl_3$).

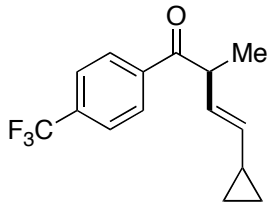
The second run was performed with (+)-**1**. The product was isolated as a colorless oil (230 mg, 75% yield) with 90% ee.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.80 (d, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 8.0 Hz, 2H), 5.67-5.62 (m, 1H), 5.50-5.44 (m, 1H), 4.05 (apparent quintet, *J* = 7.0 Hz, 1H), 2.24 (t, *J* = 7.0 Hz, 2H), 2.14 (apparent q, *J* = 7.0 Hz, 2H), 1.71-1.65 (m, 2H), 1.28 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 200.4, 135.1, 132.11 (2C), 132.05, 130.4, 130.2 (2C), 128.4, 119.7, 44.5, 31.4, 24.9, 17.6, 16.5.

IR (film) 2934, 2246, 1684, 1584, 1456, 1396, 1208, 1071, 975 cm^{-1}.

LRMS (ESI) calcd for $C_{15}H_{17}BrNO$ (M+H) 306.0, found 306.0.



(*S*,*E*)-4-Cyclopropyl-2-methyl-1-(4-(trifluoromethyl)phenyl)but-3-en-1-one (Table 2, entry 6). The title compound was prepared according to the General Procedure with 2-bromo-1-(4-(trifluoromethyl)phenyl)propan-1-one (281 mg, 1.0 mmol) and ethynylcyclopropane (132 mg, 2.0 mmol). After purification by flash chromatography (eluted with 10→30% CH_2Cl_2 in hexanes), the title compound was isolated as a colorless oil (209 mg, 78% yield) with 90% ee (HPLC analysis of the product: Daicel CHIRALPAK OJ-H column; solvent system: 10% *i*-PrOH; 1.0 mL/min; retention times: 11.3 min (major), 11.8 min (minor)).

$[\alpha]^{21}_D$ = +65 (c = 1.0, $CHCl_3$).

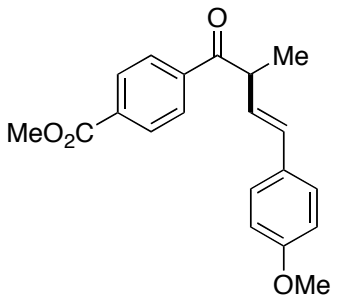
The second run was performed with (+)-**1**. The product was isolated as a colorless oil (217 mg, 81% yield) with 94% ee.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.04 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 8.0 Hz, 2H), 5.59 (dd, *J* = 15.5, 8.0 Hz, 1H), 5.07 (dd, *J* = 15.5, 8.0 Hz, 1H), 4.05 (apparent quintet, *J* = 7.0 Hz, 1H), 1.35-1.31 (m, 1H), 1.28 (d, *J* = 7.0 Hz, 3H), 0.67-0.64 (m, 2H), 0.31-0.28 (m, 2H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 200.8, 137.4 (2C), 129.1 (4C), 126.6 (2C), 125.8 (q, *J* = 15.0 Hz, 1C), 44.9, 17.5, 14.0, 6.9 (2C).

IR (film) 3009, 2934, 1689, 1456, 1410, 1130, 1067, 975, 855 cm^{-1}.

LRMS (ESI) calcd for $C_{15}H_{16}F_3O$ (M+H) 269.1, found 269.1.



(*S*,*E*)-Methyl 4-(4-(4-methoxyphenyl)-2-methylbut-3-enoyl)benzoate (Table 2, entry 7). The title compound was prepared according to the General Procedure with methyl 4-(2-bromopropanoyl)benzoate (271 mg, 1.0 mmol) and 4-ethynylanisole (264 mg, 2.0 mmol). After purification by flash chromatography (eluted with 30→70% CH_2Cl_2 in hexanes), the title compound was isolated as a colorless oil (266 mg, 82% yield) with 87% ee (SFC analysis of the product: Daicel CHIRALPAK AD-H column; solvent system: 20% MeOH; 3.0 mL/min; retention times: 9.05 min (minor), 18.57 min (major)).

$[\alpha]^{22}_D$ = –23 (c = 0.38, $CHCl_3$).

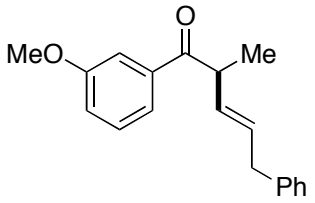
The second run was performed with (+)-**1**. The product was isolated as a colorless oil (270 mg, 83% yield) with 87% ee.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.11 (d, *J* = 8.0 Hz, 2H), 8.05 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 6.82 (d, *J* = 8.0 Hz, 2H), 6.47 (d, *J* = 16.0 Hz, 1H), 6.16 (dd, *J* = 16.0, 8.0 Hz, 1H), 4.28 (apparent quintet, *J* = 7.0 Hz, 1H), 3.94 (s, 3H), 3.79 (s, 3H), 1.41 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR ($CDCl_3$, 75 MHz) δ 200.9, 166.4, 159.4, 139.9, 133.9, 131.8, 130.0 (2C), 129.7, 128.6 (2C), 127.6 (2C), 127.0, 114.1 (2C), 55.5, 52.6, 45.5, 17.7.

IR (film) 2953, 1724, 1684, 1607, 1511, 1280, 1251, 1176, 1108, 1033, 975, 820, 725 cm^{-1}.

LRMS (ESI) calcd for $C_{20}H_{21}O_4$ (M+H) 325.1, found 325.1.



(*S*,*E*)-1-(3-Methoxyphenyl)-2-methyl-5-phenylpent-3-en-1-one (Table 2, entry 8). The title compound was prepared according to the General Procedure with 2-bromo-1-(3-methoxyphenyl)propan-1-one (243 mg, 1.0 mmol) and 3-phenyl-1-propyne (232 mg, 2.0 mmol). After purification by flash chromatography on a reverse-phase column (KP-C18-HS 30 g, Biotage SNAP Cartridge, eluted with 10→100% MeOH in hexanes), the title compound was isolated as a colorless oil (210 mg, 75% yield) with 88% ee (SFC analysis of the product: Daicel CHIRALPAK AD-H column; solvent system: 10% MeOH; 3.0 mL/min; retention times: 3.51 min (major), 4.05 min (minor)).

$[\alpha]^{22}_{D}$ = +19 (c = 1.0, $CHCl_3$).

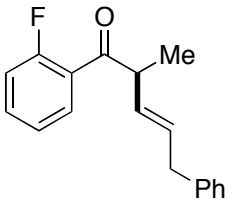
The second run was performed with (+)-**1**. The product was isolated as a colorless oil (205 mg, 73% yield) with 90% ee.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.54 (d, *J* = 7.5 Hz, 1H), 7.47 (s, 1H), 7.34 (t, *J* = 8.0 Hz, 1H), 7.23 (t, *J* = 7.5 Hz, 2H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.09-7.06 (m, 3H), 5.74-5.63 (m, 2H), 4.11 (apparent quintet, *J* = 7.0 Hz, 1H), 3.81 (s, 3H), 3.32 (d, *J* = 6.0 Hz, 2H), 1.29 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 201.6, 160.0, 140.3, 140.0, 131.6, 131.5, 129.7, 128.7 (2C), 128.6 (2C), 126.3, 121.4, 119.6, 113.0, 55.6, 44.9, 39.1, 17.8.

IR (film) 2931, 1725, 1688, 1597, 1488, 1455, 1262, 1123, 1041, 744, 699 cm^{-1}.

LRMS (ESI) calcd for $C_{19}H_{21}O_2$ (M+H) 281.1, found 281.1.



(*S*,*E*)-1-(2-Fluorophenyl)-2-methyl-5-phenylpent-3-en-1-one (Table 2, entry 9). The title compound was prepared according to the General Procedure with 2-bromo-1-(2-fluorophenyl) propan-1-one (230 mg, 1.0 mmol) and 3-phenyl-1-propyne (232 mg, 2.0 mmol). After purification by flash chromatography (eluted with 30→70% CH_2Cl_2 in hexanes), the title compound was isolated as a colorless oil (241 mg, 90% yield) with 81% ee (SFC analysis of the product: Daicel CHIRALPAK AD-H column; solvent system: 5.0% MeOH; 3.0 mL/min; retention times: 2.85 min (minor), 3.27 min (major)).

$[\alpha]^{22}_{D}$ = +50 (c = 1.0, $CHCl_3$).

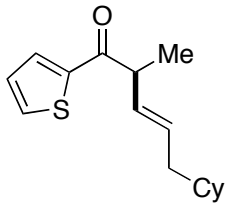
The second run was performed with (+)-**1**. The product was isolated as a colorless oil (247 mg, 92% yield) with 81% ee.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.77 (td, *J* = 7.5, 1.8 Hz, 1H), 7.54-7.46 (m, 1H), 7.27-7.03 (m, 7H), 5.76-5.59 (m, 2H), 4.05 (apparent quintet, *J* = 6.5 Hz, 1H), 3.33 (d, *J* = 6.5 Hz, 2H), 1.33 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 201.0, 161.0 (d, *J* = 220 Hz), 140.3, 134.2 (d, *J* = 8.9 Hz), 131.7, 131.1 (d, *J* = 2.9 Hz), 130.7, 128.56 (2C), 128.52 (3C), 126.2, 124.6 (d, *J* = 3.5 Hz), 116.7 (d, *J* = 24 Hz), 49.2 (d, *J* = 6.3 Hz), 39.1, 16.9.

IR (film) 2931, 1685, 1609, 1451, 1272, 1211, 1099, 975, 752, 698 cm^{-1}.

LRMS (ESI) calcd for $C_{18}H_{18}FO$ (M+H) 269.1, found 269.1.



(*S*,*E*)-5-Cyclohexyl-2-methyl-1-(thiophen-2-yl)pent-3-en-1-one (Table 2, entry 10). The title compound was prepared according to the General Procedure with 2-bromo-1-(thiophen-2-yl)-propan-1-one (219 mg, 1.0 mmol) and prop-2-ynylcyclohexane (244 mg, 2.0 mmol). After purification by flash chromatography (eluted with 20→50% CH_2Cl_2 in hexanes), the title compound was isolated as a colorless oil (220 mg, 84% yield) with 94% ee (HPLC analysis of the product: Daicel CHIRALPAK IC-H column; solvent system: 5.0% *i*-PrOH; 1.0 mL/min; retention times: 13.4 min (major), 14.6 min (minor)).

$[\alpha]^{22}_D$ = +59 (c = 1.0, $CHCl_3$).

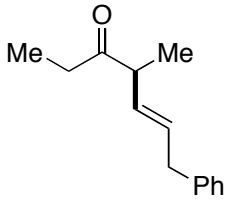
The second run was performed with (+)-**1**. The product was isolated as a colorless oil (226 mg, 86% yield) with 94% ee.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.74 (d, *J* = 4.0 Hz, 1H), 7.59 (d, *J* = 5.0 Hz, 1H), 7.10 (dd, *J* = 7.0, 5.0 Hz, 1H), 5.60-5.55 (m, 1H), 5.52-5.47 (m, 1H), 3.91 (apparent quintet, *J* = 7.0 Hz, 1H), 1.88-1.85 (m, 2H), 1.65-1.59 (m, 5H), 1.29 (d, *J* = 7.0 Hz, 3H), 1.24-1.06 (m, 4H), 0.84-0.79 (m, 2H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 194.8, 143.9, 133.7, 132.2, 131.9, 130.8, 128.2, 46.8, 40.7, 38.0, 33.21, 33.17, 26.7, 26.5 (2C), 17.8.

IR (film) 2922, 1668, 1518, 1448, 1415, 1236, 1055, 970, 853, 721 cm^{-1}.

LRMS (ESI) calcd for $C_{16}H_{23}OS$ (M+H) 263.1, found 263.1.



(*S*,*E*)-4-Methyl-7-phenylhept-5-en-3-one (Table 3, entry 1). The title compound was prepared according to the General Procedure with 2-bromopentan-3-one (165 mg, 1.0 mmol) and 3-phenyl-1-propyne (232 mg, 2.0 mmol). After purification by flash chromatography (eluted with 20→50% CH_2Cl_2 in hexanes), the title compound was isolated as a colorless oil (178 mg, 88% yield) with 91% ee (SFC analysis of the product: Daicel CHIRALPAK AS-H column; solvent system: 2.5% MeOH; 3.0 mL/min; retention times: 2.91 min (minor), 3.05 min (major)).

$[\alpha]^{22}_D$ = +89 (c = 1.0, $CHCl_3$).

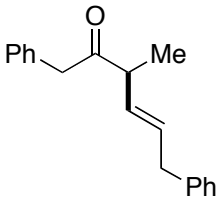
The second run was performed with (+)-**1**. The product was isolated as a colorless oil (170 mg, 84% yield) with 89% ee.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.27 (t, *J* = 7.5 Hz, 2H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.14 (d, *J* = 7.5 Hz, 2H), 5.74-5.67 (m, 1H), 5.51-5.46 (m, 1H), 3.34 (d, *J* = 6.5 Hz, 2H), 3.19 (apparent quintet, *J* = 7.0 Hz, 1H), 2.55-2.48 (m, 1H), 2.45-2.39 (m, 1H), 1.15 (d, *J* = 7.0 Hz, 3H), 1.01 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 212.8, 140.3, 131.7, 131.0, 128.7 (4C), 126.3, 50.3, 39.2, 34.1, 16.6, 8.0.

IR (film) 2974, 1717, 1558, 1495, 1456, 1374, 974, 699 cm^{-1}.

LRMS (ESI) calcd for $C_{14}H_{19}O$ (M+H) 203.1, found 203.1.



(*S*,*E*)-3-Methyl-1,6-diphenylhex-4-en-2-one (Table 3, entry 2). The title compound was prepared according to the General Procedure with 3-bromo-1-phenylbutan-2-one (227 mg, 1.0 mmol) and 3-phenyl-1-propyne (232 mg, 2.0 mmol). After purification by flash chromatography (eluted with 20→50% CH_2Cl_2 in hexanes), the title compound was isolated as a colorless oil (220 mg, 83% yield) with 80% ee (SFC analysis of the product: Daicel CHIRALPAK AD-H column; solvent system: 2.5% MeOH; 3.0 mL/min; retention times: 6.12 min (major), 6.94 min (minor)).

$[\alpha]^{21}_D$ = +99 (c = 1.0, $CHCl_3$).

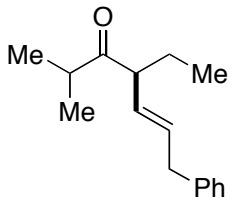
The second run was performed with (+)-**1**. The product was isolated as a colorless oil (211 mg, 80% yield) with 80% ee.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.34-7.14 (m, 10H), 5.77-5.72 (m, 1H), 5.53-5.47 (m, 1H), 3.77 (s, 2H), 3.39 (d, *J* = 7.0 Hz, 2H), 3.37-3.33 (m, 1H), 1.17 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR ($CDCl_3$, 75 MHz) δ 209.1, 140.1, 134.4, 132.4, 130.5, 129.7 (2C), 128.7 (2C), 128.6 (4C), 127.0, 126.3, 49.7, 47.9, 39.1, 16.4.

IR (film) 3027, 1716, 1558, 1495, 1455, 1030, 970, 697 cm^{-1}.

LRMS (ESI) calcd for $C_{19}H_{21}O$ (M+H) 265.2, found 265.2.



(*S*,*E*)-4-Ethyl-2-methyl-7-phenylhept-5-en-3-one (Table 3, entry 3). The title compound was prepared according to the General Procedure with 4-bromo-2-methylhexan-3-one (193 mg, 1.0 mmol) and 3-phenyl-1-propyne (232 mg, 2.0 mmol). After purification by flash chromatography (eluted with 20→50% CH_2Cl_2 in hexanes), the title compound was isolated as a colorless oil (184 mg, 80% yield) with 98% ee (SFC analysis of the product: Daicel CHIRALCEL OJ column; solvent system: 5.0% MeOH; 3.0 mL/min; retention times: 4.37 min (major), 4.89 min (minor)).

$[\alpha]^{21}_D$ = +149 (c = 1.0, $CHCl_3$).

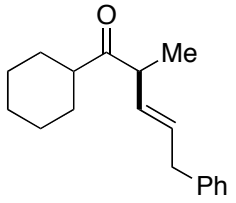
The second run was performed with (+)-**1**. The product was isolated as a colorless oil (193 mg, 84% yield) with 98% ee.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.26 (t, *J* = 7.5 Hz, 2H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.13 (d, *J* = 7.5 Hz, 2H), 5.71-5.65 (m, 1H), 5.37 (dd, *J* = 15.0, 9.0 Hz, 1H), 3.34 (d, *J* = 7.0 Hz, 2H), 3.13 (q, *J* = 7.5 Hz, 1H), 2.75-2.70 (m, 1H), 1.75-1.69 (m, 1H), 1.46-1.42 (m, 1H), 1.04 (d, *J* = 7.0 Hz, 3H), 1.03 (d, *J* = 7.0 Hz, 3H), 0.83 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 215.4, 140.3, 132.6, 130.0, 128.61 (2C), 128.60 (2C), 126.3, 56.7, 39.9, 39.2, 24.8, 18.6, 18.2, 12.1.

IR (film) 2967, 1711, 1494, 1453, 1381, 1029, 972, 746, 698 cm^{-1}.

LRMS (ESI) calcd for $C_{16}H_{23}O$ (M+H) 231.2, found 232.2.



(*S*,*E*)-1-Cyclohexyl-2-methyl-5-phenylpent-3-en-1-one (Table 3, entry 4). The title compound was prepared according to the General Procedure with 2-bromo-1-cyclohexylpropan-1-one (219 mg, 1.0 mmol) and 3-phenyl-1-propyne (232 mg, 2.0 mmol). After

purification by flash chromatography (eluted with 20→50% CH_2Cl_2 in hexanes), the title compound was isolated as a colorless oil (231 mg, 90% yield) with 91% ee (SFC analysis of the product: Daicel CHIRALPAK AD-H column; solvent system: 2.5% MeOH; 3.0 mL/min; retention times: 4.18 min (major), 4.47 min (minor)).

$[\alpha]^{21}_D$ = +128 (c = 1.0, $CHCl_3$).

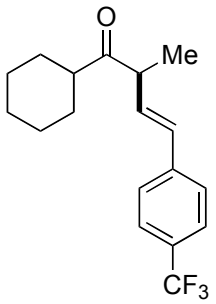
The second run was performed with (+)-**1**. The product was isolated as a colorless oil (215 mg, 84% yield) with 90% ee.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.27 (t, *J* = 7.5 Hz, 2H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.14 (d, *J* = 7.5 Hz, 2H), 5.74-5.68 (m, 1H), 5.49-5.44 (m, 1H), 3.35 (d, *J* = 7.0 Hz, 2H), 3.34-3.30 (m, 1H), 2.55-2.51 (m, 1H), 1.79-1.69 (m, 4H), 1.66-1.64 (m, 1H), 1.38-1.34 (m, 1H), 1.26-1.18 (m, 4H), 1.14 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR ($CDCl_3$, 75 MHz) δ 215.0, 140.3, 131.6, 131.0, 128.61 (2C), 128.58 (2C), 126.3, 49.2, 48.9, 39.1, 29.1, 28.5, 26.0 (2C), 25.6, 16.7.

IR (film) 2930, 1708, 1495, 1451, 1372, 1144, 990, 971, 698 cm^{-1}.

LRMS (ESI) calcd for $C_{18}H_{25}O$ (M+H) 257.2, found 257.2.



(*S*,*E*)-1-Cyclohexyl-2-methyl-4-(4-(trifluoromethyl)phenyl)but-3-en-1-one (Table 3, entry 5). The title compound was prepared according to the General Procedure, except that the reaction was conducted at 40 °C for 48 h, with 2-bromo-1-cyclohexylpropan-1-one (219 mg, 1.0 mmol) and 4-ethynyl-α,α,α-trifluorotoluene (340 mg, 2.0 mmol). After purification by flash chromatography (eluted with 20→50% CH_2Cl_2 in hexanes), the title compound was isolated as a colorless oil (267 mg, 86% yield) with 90% ee (SFC analysis of the product: Daicel CHIRALPAK AD-H column; solvent system: 2.5% MeOH; 3.0 mL/min; retention times: 3.89 min (major), 4.14 min (minor)).

$[\alpha]^{21}_D$ = +18 (c = 1.0, $CHCl_3$).

The second run was performed with (+)-**1**. The product was isolated as a colorless oil (255 mg, 82% yield) with 90% ee.

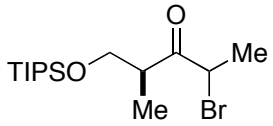
^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.54 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 6.48 (d, *J* = 16.0 Hz, 1H), 6.26 (dd, *J* = 16.0, 6.5 Hz, 1H), 3.54 (apparent quintet, *J* = 6.5 Hz, 1H), 2.57-2.49 (m, 1H), 1.76-1.58 (m, 6H), 1.42-1.04 (m, 4H), 1.25 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 214.2, 140.6, 132.4, 130.4, 126.6 (4C), 126.2, 125.7 (q, J = 37.5 Hz), 49.9, 49.0, 29.0, 28.5, 25.98, 25.95, 25.7, 17.2.

IR (film) 2932, 1709, 1616, 1494, 1451, 1325, 1124, 1067 cm^{-1}.

LRMS (ESI) calcd for $C_{18}H_{22}F_3O$ (M+H) 311.2, found 311.2.

III. Asymmetric Cross-Couplings (eq 2 and eq 3)



(2*S*)-4-Bromo-2-methyl-1-(triisopropylsilyloxy)pentan-3-one (A). A 100-mL round-bottomed flask equipped with a stir bar was charged with (*S*)-2-methyl-1-(triisopropylsilyloxy)pentan-3-one[6] (1.09 g, 4.0 mmol) and THF (10 mL). The solution was cooled to –78 °C in a dry-ice bath, and then a solution of LiHMDS in hexanes (1.0 M; 4.0 mL, 4.0 mmol) was added by syringe over 4 min. After the addition was complete, the dry-ice bath was removed, and the reaction flask was placed in an ice bath. The reaction mixture was stirred at 0 °C for 10 min, and then it was cooled to –78 °C and bromine (206 μL, 4.0 mmol) was added dropwise over 2.0 min. After the addition was complete, the reaction mixture was stirred for 2 min, and then it was poured into a saturated aqueous solution of $NaHCO_3$ (20 mL) and extracted with ether (20 mL×3). The combined organic layers were successively washed with water (20 mL), a saturated aqueous solution of $Na_2S_2O_3$ (20 mL), and brine (20 mL). The organic solution was dried over $MgSO_4$, filtered, and concentrated by rotary evaporation. The residue was purified by flash chromatography on silica gel (eluted with 10→30% CH_2Cl_2 in hexanes), which furnished a colorless oil (1.21 g, 86% yield) as a 1:1 mixture of diastereomers.

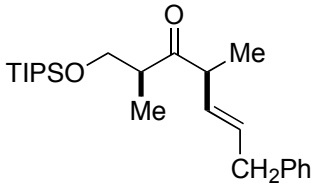
^{1}H NMR ($CDCl_3$, 500 MHz; 1:1 mixture of diastereomers) δ 4.57 (q, J = 6.5 Hz, 1H), 4.52 (d, J = 6.5 Hz, 1H), 3.90 (dd, J = 9.0, 7.0 Hz, 1H), 3.71-3.67 (m, 2H), 3.64 (dd, J = 12.5, 6.0 Hz, 1H), 3.29-3.25 (m, 1H), 3.19-3.15 (m, 1H), 1.72 (d, J = 6.5 Hz, 3H), 1.66 (d, J = 6.5 Hz, 3H), 1.12 (d, J = 6.5 Hz, 3H), 1.05 (d, J = 6.5 Hz, 3H), 1.01-0.98 (m, 42H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 207.5, 206.9, 68.1, 66.0, 49.3, 47.8, 46.0, 45.6, 20.4, 19.1, 18.17 (3C), 18.15 (3C), 18.12 (3C), 18.10 (3C), 15.0, 13.7, 12.1 (3C), 12.0 (3C).

IR (film) 2943, 2867, 1719, 1463, 1383, 1094, 882, 795 cm^{-1}.

LRMS (EI) calcd for $C_{15}H_{32}BrO_2Si$ (M+H) 351.1, found 351.1.

(6) Denmark, S. E.; Fujimori, S. *Org. Lett.* **2002**, *4*, 3473–3476.



(2*S*,4*S*,*E*)-2,4-Dimethyl-7-phenyl-1-(triisopropylsilyloxy)hept-5-en-3-one (eq 2). The title compound was prepared according to the General Procedure with ketone **A** (176 mg, 0.50 mmol), 3-phenyl-1-propyne (116 mg, 1.0 mmol), $NiCl_2$•glyme (5.5 mg, 0.025 mmol), ligand (–)-**1** (14.7 mg, 0.030 mmol), and DME (4.0 mL). After purification by flash chromatography (eluted with 10→30% CH_2Cl_2 in hexanes), the title compound was isolated as a colorless oil (161 mg, 83% yield) with 15:1 dr (determined by ^{1}H NMR).

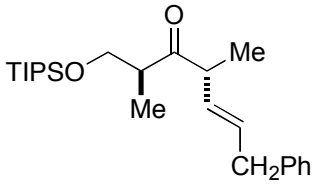
$[\alpha]^{22}_D$ = +95 (c = 1.0, $CHCl_3$).

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.30 (t, *J* = 8.0 Hz, 2H), 7.21 (t, *J* = 8.0 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 2H), 5.80-5.75 (m, 1H), 5.49-5.44 (m, 1H), 3.80 (t, *J* = 9.0 Hz, 2H), 3.66 (dd, *J* = 9.0, 5.0 Hz, 1H), 3.41 (apparent quintet, *J* = 7.0 Hz, 1H), 3.37 (d, *J* = 6.5 Hz, 2H), 3.11-3.07 (m, 1H), 1.16 (d, *J* = 6.5 Hz, 3H), 1.06-1.03 (m, 20H), 0.96 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 215.2, 140.7, 132.7, 130.9, 129.08 (2C), 129.05 (2C), 126.7, 67.5, 52.0, 47.3, 39.6, 18.57 (3C), 18.55 (3C), 16.2, 13.9, 12.4 (3C).

IR (film) 2942, 1716, 1463, 1382, 1097, 997, 882 cm^{-1}.

LRMS (ESI) calcd for $C_{24}H_{41}O_2Si$ (M+H) 389.3, found 389.3.



(2*S*,4*R*,*E*)-2,4-Dimethyl-7-phenyl-1-(triisopropylsilyloxy)hept-5-en-3-one (eq 3) The title compound was prepared according to the General Procedure with ketone **A** (176 mg, 0.50 mmol), 3-phenyl-1-propyne (116 mg, 1.0 mmol), $NiCl_2$•glyme (5.5 mg, 0.025 mmol), ligand (+)-**1** (14.7 mg, 0.030 mmol), and DME (4.0 mL). After purification by flash chromatography (eluted with 10→50% benzene in hexanes), the title compound was isolated as a colorless oil (155 mg, 80% yield) with 10:1 dr (determined by ^{1}H NMR).

$[\alpha]^{22}_D$ = –29 (c = 1.0, $CHCl_3$).

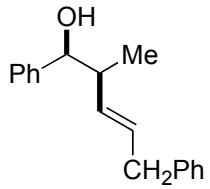
^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.29 (t, *J* = 7.5 Hz, 2H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.17 (d, *J* = 7.5 Hz, 2H), 5.78-5.69 (m, 1H), 5.58-5.53 (dd, *J* = 15.0, 7.0 Hz, 1H), 3.91 (dd, *J* = 9.5, 7.0 Hz, 1H), 3.61 (dd, *J* = 9.5, 6.0 Hz, 1H), 3.39-3.35 (m, 3H), 3.05-3.01 (m, 1H), 1.19 (d, *J* = 7.0 Hz, 3H), 1.11-1.04 (m, 24H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 214.8, 140.4, 131.6, 130.7, 128.7 (2C), 128.6 (2C), 126.3, 66.5, 49.9, 47.1, 39.2, 18.19 (3C), 18.14 (3C), 16.6, 13.3, 12.1 (3C).

IR (film) 2942, 1715, 1462, 1382, 1100, 998, 882 cm^{-1}.

LRMS (ESI) calcd for $C_{24}H_{41}O_2Si$ (M+H) 389.3, found 389.3.

IV. Stereoselective Reduction (eq 4)



(1*S*,2*S*,*E*)-2-Methyl-1,5-diphenylpent-3-en-1-ol (eq 4). Lithium aluminum hydride (1.0 M in diethyl ether; 0.88 mL, 0.88 mmol) was added dropwise by syringe over 3.0 min to a 25-mL round-bottomed flask equipped with a stir bar and charged with (*S*,E)-2-methyl-1,5-diphenylpent-3-en-1-one (200 mg, 0.80 mmol; 92% ee) and THF (8 mL) at –78 °C. The reaction mixture was stirred at –78 °C for 1.0 h and then at –20 °C for 1.0 h. Next, the reaction was quenched by the dropwise addition of water (1.0 mL) over 5 min at –20 °C. The solution was warmed to rt and poured into a mixture of diethyl ether (25 mL) and aqueous HCl (1.0 N; 25 mL). The organic layer was separated, and the aqueous layer was extracted with diethyl ether (25 mL×3). The organic layers were combined, dried over anhydrous sodium sulfate, and filtered. The filtrate was concentrated by rotary evaporation, and the residue was subjected to flash chromatography on silica gel (eluted with 50→100% CH_2Cl_2 in hexanes), which furnished the title compound as a colorless oil (192 mg, 95% yield; 10:1 dr (determined by ^1H NMR); major diastereomer: 90% ee (SFC analysis of the product: Daicel CHIRALPAK AD-H column; solvent system: 5.0% MeOH; 3.0 mL/min; retention times: 7.95 min (minor), 9.42 min (major)).

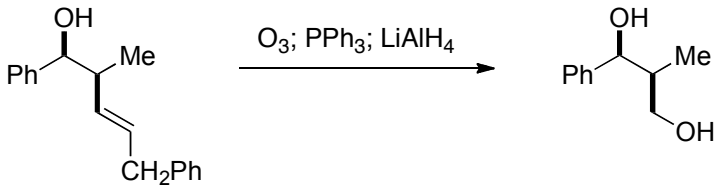
$[\alpha]^{22}_D$ = –93 (c = 1.0, $CHCl_3$).

^1H NMR ($CDCl_3$, 500 MHz) δ 7.33-7.24 (m, 7H), 7.20-7.14 (m, 3H), 5.77-5.71 (m, 1H), 5.50-5.44 (m, 1H), 4.33 (dd, *J* = 8.0, 2.0 Hz, 1H), 3.38 (d, *J* = 7.0 Hz, 2H), 2.47-2.42 (m, 1H), 2.12 (d, *J* = 2.0 Hz, 1H), 0.86 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 142.7, 140.6, 133.7, 132.1, 128.7 (4C), 128.5 (2C), 127.8, 127.1 (2C), 126.3, 78.3, 45.6, 39.3, 17.3.

IR (film) 3421, 3027, 1603, 1494, 1452, 1028, 973, 746, 699 cm^{-1}.

LRMS (EI) calcd for $C_{18}H_{21}O$ (M+H) 253.2, found 253.2.



Determination of relative stereochemistry. (1*S*,2*S*)-2-Methyl-1-phenylpropane-1,3-diol. Ozone was bubbled for 5 min into a 25-mL round-bottomed flask equipped with a stir bar and charged with (1*S*,2*S*,*E*)-2-methyl-1,5-diphenylpent-3-en-1-ol (50 mg, 0.20 mmol) and anhydrous CH_2Cl_2 (5 mL) at –78 °C, during which time the solution turned from colorless to light blue. Next, argon was bubbled through the solution for 5 min, during which time the solution turned from blue to colorless. Then, PPh_3 (63 mg, 0.24 mmol) was added to the flask in one portion, and the solution was warmed to 0 °C in an ice bath and stirred for 10 min. The resulting mixture was then cooled to –78 °C, and then a solution of lithium aluminum hydride (1.0 M in diethyl ether; 0.60 mL, 0.60 mmol) was added dropwise over 3 min. The reaction mixture was stirred at –78 °C for 1.0 h, and then it was placed in a 0 °C ice bath for 10 min. The reaction was quenched by the dropwise addition of water (1.0 mL) over 5 min at 0 °C. The solution was warmed to rt and poured into a mixture of diethyl ether (15 mL) and aqueous HCl (1.0 N; 15 mL). The organic layer was separated, and the aqueous layer was extracted with diethyl ether (15 mL×3). The organic layers were combined, dried over anhydrous sodium sulfate, and filtered. The filtrate was concentrated by rotary evaporation, and the residue was subjected to flash chromatography on silica gel (eluted with 50% EtOAc in hexanes), which furnished the title compound as a colorless oil (32.0 mg, 96% yield) with 90% ee (SFC analysis of the product: Daicel CHIRALCEL OD-H column; solvent system: 5.0% MeOH; 3.0 mL/min; retention times: 10.5 min (major), 11.0 min (minor)).

$[\alpha]^{22}_D$ = –44 (c = 1.0, $CHCl_3$); lit.[7] $[\alpha]^{20}_D$ = –43 (c = 0.7, $CHCl_3$; the ee was not reported); lit.[8] $[\alpha]^{20}_D$ = –51 (c = 0.6, $CHCl_3$; >98% ee); lit.[9] $[\alpha]^{20}_D$ = –44 (c = 1.04, $CHCl_3$; 89% ee).

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.35-7.24 (m, 5H), 4.54 (d, *J* = 8.0 Hz, 1H), 3.75-3.69 (m, 2H), 2.80 (s, 1H), 2.06-2.04 (m, 1H), 0.69 (d, *J* = 7.0 Hz, 3H).

The spectral data are in agreement with the reported values.[7,8]

V. Assignment of Absolute Configuration

The absolute configuration of the product from entry 3 of Table 1 (run 1) was determined in Section IV.

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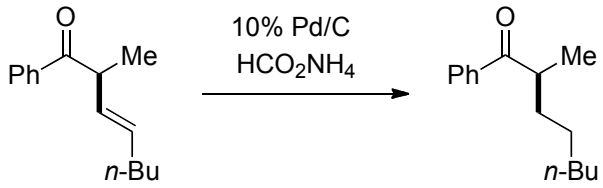
(7) Fang, G. Y.; Aggarwal, V. K. *Angew. Chem., Int. Ed.* **2007**, *46*, 359–362.

(8) Pietruszka, J.; Schöne, N. *Eur. J. Org. Chem.* **2004**, 5011–5019.

(9) Abiko, A.; Liu, J.-F.; Masamune, S. *J. Am. Chem. Soc.* **1997**, *119*, 2586–2587.



Product from entry 2 of Table 1 (run 1). (*S*)-2-Methyl-1-phenyloctan-1-one. A mixture of (*S*,*E*)-2-methyl-1-phenyloct-3-en-1-one (50 mg, 0.231 mmol), ammonium formate (145 mg, 2.31 mmol), anhydrous MeOH (5.0 mL), and Pd/C (24.6 mg, 10 wt%) in a 10-mL round-bottomed flask was refluxed for 2 h under Ar. The black solution was then filtered through celite in a Büchner funnel. The celite was washed with additional MeOH (10 mL), and the organic filtrate was concentrated by rotary evaporation. The residue was subjected to flash chromatography on silica gel (eluted with 20→40% CH_2Cl_2 in hexanes), which furnished the product as a colorless oil (41.4 mg, 82% yield) with 40% ee (HPLC analysis of the product: Daicel CHIRALPAK IC column; solvent system: 1.0% *i*-PrOH; 1.0 mL/min; retention times: 7.59 min (major), 7.98 min (minor)).

$[\alpha]^{21}_D$ = +10 (c = 1.2, diethyl ether); lit.[10] $[\alpha]^{20}_D$ = –20 (c = 4.9, diethyl ether; (*R*)-enantiomer, 90% ee); lit.[11] $[\alpha]^{20}_D$ = –22 (c = 5.0, diethyl ether; (*R*) enantiomer, optical purity was not reported).

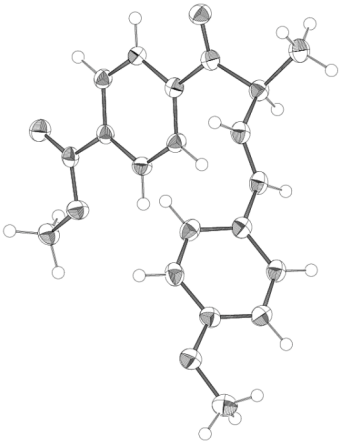
^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.95 (d, *J* = 8.0 Hz, 2H), 7.55 (t, *J* = 8.0 Hz, 1H), 7.45 (t, *J* = 8.0 Hz, 2H), 3.50-3.39 (m, 1H), 1.83-1.72 (m, 1H), 1.47-1.33 (m, 1H), 1.30-1.21 (m, 8H), 1.19 (d, *J* = 7.0 Hz, 3H), 0.82 (t, *J* = 7.0 Hz, 3H).

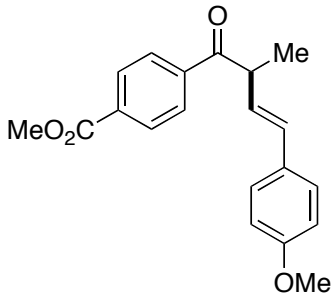
A racemic sample of the product was obtained by alkylation of propiophenone with 1-iodohexane.

(10) Koga, T.; Makinouchi, S.; Okukado, N. *Chem. Lett.* **1988**, 1141–1144.

(11) Seebach, D.; Steinmüller, D.; Demuth, F. *Angew. Chem., Int. Ed.* **1968**, *7*, 620–621.

Product from entry 7 of Table 2 (run 1). (*S*,*E*)-Methyl 4-(4-(4-methoxyphenyl)-2-methylbut-3-enoyl)benzoate.





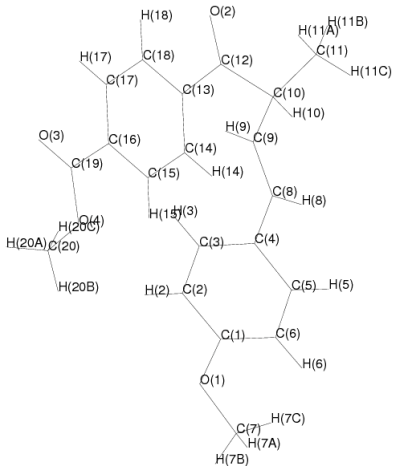


Table 1. Crystal data and structure refinement for d09054.

Identification code	d09054	
Empirical formula	C20 H20 O4	
Formula weight	324.36	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 6.01380(10) Å	α= 90°.
	b = 23.3983(4) Å	β= 93.1990(10)°.
	c = 17.9273(3) Å	γ = 90°.
Volume	2518.67(7) $Å^3$	
Z	6	
Density (calculated)	1.283 Mg/m^3	
Absorption coefficient	0.721 mm^{-1}	
F(000)	1032	
Crystal size	0.50 x 0.10 x 0.05 mm^3	
Theta range for data collection	2.47 to 67.71°.	
Index ranges	-7<=h<=6, -28<=k<=28, -21<=l<=21	
Reflections collected	36378	
Independent reflections	8828 [R(int) = 0.0321]	
Completeness to theta = 67.71°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9648 and 0.7144	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8828 / 1 / 658	
Goodness-of-fit on F^2	1.029	
Final R indices [I>2sigma(I)]	R1 = 0.0320, wR2 = 0.0804	
R indices (all data)	R1 = 0.0350, wR2 = 0.0827	
Absolute structure parameter	0.09(10)	
Largest diff. peak and hole	0.239 and -0.139 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for d09054. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	6714(2)	7130(1)	10229(1)	32(1)
O(2)	15607(2)	7576(1)	5979(1)	31(1)
O(3)	11039(2)	10320(1)	5595(1)	33(1)
O(4)	8018(2)	9988(1)	6130(1)	29(1)
C(1)	7345(3)	7078(1)	9509(1)	27(1)
C(2)	9274(3)	7374(1)	9343(1)	30(1)
C(3)	10054(3)	7350(1)	8634(1)	28(1)
C(4)	8921(3)	7034(1)	8062(1)	25(1)
C(5)	7004(3)	6746(1)	8244(1)	27(1)
C(6)	6203(3)	6760(1)	8957(1)	28(1)
C(7)	4650(3)	6868(1)	10400(1)	36(1)
C(8)	9614(3)	7030(1)	7286(1)	26(1)
C(9)	11645(3)	7114(1)	7053(1)	26(1)
C(10)	12147(3)	7128(1)	6232(1)	27(1)
C(11)	13251(3)	6572(1)	5987(1)	36(1)
C(12)	13637(3)	7638(1)	6076(1)	25(1)
C(13)	12637(3)	8230(1)	6052(1)	23(1)
C(14)	10542(3)	8352(1)	6304(1)	24(1)
C(15)	9711(3)	8904(1)	6274(1)	24(1)
C(16)	10959(3)	9344(1)	5975(1)	22(1)
C(17)	13059(3)	9224(1)	5720(1)	24(1)
C(18)	13898(3)	8671(1)	5761(1)	24(1)
C(19)	10056(3)	9936(1)	5879(1)	23(1)
C(20)	6948(3)	10536(1)	5997(1)	30(1)
O(5)	467(2)	8657(1)	12117(1)	28(1)
O(6)	8247(2)	9331(1)	7975(1)	34(1)
O(7)	4489(2)	12143(1)	7707(1)	35(1)
O(8)	1016(2)	11803(1)	7526(1)	36(1)
C(21)	1192(3)	8673(1)	11407(1)	25(1)
C(22)	139(3)	8970(1)	10813(1)	29(1)
C(23)	1073(3)	8965(1)	10118(1)	32(1)
C(24)	3044(3)	8668(1)	10002(1)	29(1)

C(25)	4030(3)	8369(1)	10603(1)	30(1)
C(26)	3137(3)	8367(1)	11293(1)	29(1)
C(27)	-1572(3)	8949(1)	12242(1)	35(1)
C(28)	4103(3)	8653(1)	9277(1)	31(1)
C(29)	3466(3)	8931(1)	8666(1)	31(1)
C(30)	4644(3)	8895(1)	7934(1)	25(1)
C(31)	5862(3)	8333(1)	7816(1)	31(1)
C(32)	6242(3)	9401(1)	7909(1)	24(1)
C(33)	5328(3)	9999(1)	7827(1)	23(1)
C(34)	6809(3)	10449(1)	7983(1)	25(1)
C(35)	6113(3)	11011(1)	7904(1)	27(1)
C(36)	3924(3)	11131(1)	7666(1)	25(1)
C(37)	2438(3)	10686(1)	7503(1)	25(1)
C(38)	3130(3)	10121(1)	7589(1)	23(1)
C(39)	3219(3)	11745(1)	7630(1)	27(1)
C(40)	198(4)	12387(1)	7569(1)	43(1)
O(9)	8990(2)	10429(1)	-387(1)	36(1)
O(10)	5370(2)	10189(1)	4243(1)	33(1)
O(11)	10347(2)	7507(1)	4574(1)	38(1)
O(12)	7000(2)	7132(1)	4236(1)	39(1)
C(41)	8063(3)	10422(1)	290(1)	27(1)
C(42)	6176(3)	10077(1)	339(1)	31(1)
C(43)	5146(3)	10032(1)	1008(1)	29(1)
C(44)	5963(3)	10326(1)	1650(1)	25(1)
C(45)	7818(3)	10671(1)	1580(1)	27(1)
C(46)	8872(3)	10726(1)	914(1)	27(1)
C(47)	10860(4)	10794(1)	-467(1)	44(1)
C(48)	4978(3)	10272(1)	2380(1)	28(1)
C(49)	3353(3)	9931(1)	2564(1)	28(1)
C(50)	2491(3)	9907(1)	3349(1)	27(1)
C(51)	1243(3)	10448(1)	3558(1)	34(1)
C(52)	4504(3)	9801(1)	3884(1)	26(1)
C(53)	5467(3)	9207(1)	3952(1)	25(1)
C(54)	4302(3)	8717(1)	3712(1)	28(1)
C(55)	5230(3)	8179(1)	3842(1)	30(1)
C(56)	7361(3)	8132(1)	4190(1)	27(1)
C(57)	8553(3)	8621(1)	4403(1)	27(1)
C(58)	7597(3)	9153(1)	4293(1)	26(1)

C(59)	8424(3)	7564(1)	4354(1)	30(1)
C(60)	7910(4)	6567(1)	4414(1)	45(1)

Table 3. Bond lengths [Å] and angles [°] for d09054.

O(1)-C(1)	1.372(2)
O(1)-C(7)	1.432(2)
O(2)-C(12)	1.216(2)
O(3)-C(19)	1.204(2)
O(4)-C(19)	1.334(2)
O(4)-C(20)	1.449(2)
C(1)-C(6)	1.390(3)
C(1)-C(2)	1.397(3)
C(2)-C(3)	1.381(3)
C(2)-H(2)	0.9500
C(3)-C(4)	1.408(3)
C(3)-H(3)	0.9500
C(4)-C(5)	1.390(3)
C(4)-C(8)	1.474(2)
C(5)-C(6)	1.390(3)
C(5)-H(5)	0.9500
C(6)-H(6)	0.9500
C(7)-H(7A)	0.9800
C(7)-H(7B)	0.9800
C(7)-H(7C)	0.9800
C(8)-C(9)	1.328(3)
C(8)-H(8)	0.9500
C(9)-C(10)	1.519(2)
C(9)-H(9)	0.9500
C(10)-C(12)	1.529(2)
C(10)-C(11)	1.536(3)
C(10)-H(10)	1.0000
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-C(13)	1.509(2)
C(13)-C(14)	1.392(2)
C(13)-C(18)	1.398(2)
C(14)-C(15)	1.385(2)
C(14)-H(14)	0.9500
C(15)-C(16)	1.398(2)

C(15)-H(15)	0.9500
C(16)-C(17)	1.395(2)
C(16)-C(19)	1.495(2)
C(17)-C(18)	1.390(2)
C(17)-H(17)	0.9500
C(18)-H(18)	0.9500
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
O(5)-C(21)	1.369(2)
O(5)-C(27)	1.432(2)
O(6)-C(32)	1.216(2)
O(7)-C(39)	1.208(2)
O(8)-C(39)	1.334(2)
O(8)-C(40)	1.455(2)
C(21)-C(22)	1.394(3)
C(21)-C(26)	1.396(3)
C(22)-C(23)	1.394(3)
C(22)-H(22)	0.9500
C(23)-C(24)	1.399(3)
C(23)-H(23)	0.9500
C(24)-C(25)	1.390(3)
C(24)-C(28)	1.479(3)
C(25)-C(26)	1.377(3)
C(25)-H(25)	0.9500
C(26)-H(26)	0.9500
C(27)-H(27A)	0.9800
C(27)-H(27B)	0.9800
C(27)-H(27C)	0.9800
C(28)-C(29)	1.313(3)
C(28)-H(28)	0.9500
C(29)-C(30)	1.527(2)
C(29)-H(29)	0.9500
C(30)-C(31)	1.526(2)
C(30)-C(32)	1.527(2)
C(30)-H(30)	1.0000
C(31)-H(31A)	0.9800
C(31)-H(31B)	0.9800

C(31)-H(31C)	0.9800
C(32)-C(33)	1.507(2)
C(33)-C(38)	1.396(3)
C(33)-C(34)	1.397(2)
C(34)-C(35)	1.384(3)
C(34)-H(34)	0.9500
C(35)-C(36)	1.390(3)
C(35)-H(35)	0.9500
C(36)-C(37)	1.392(3)
C(36)-C(39)	1.499(2)
C(37)-C(38)	1.391(2)
C(37)-H(37)	0.9500
C(38)-H(38)	0.9500
C(40)-H(40A)	0.9800
C(40)-H(40B)	0.9800
C(40)-H(40C)	0.9800
O(9)-C(41)	1.364(2)
O(9)-C(47)	1.426(2)
O(10)-C(52)	1.213(2)
O(11)-C(59)	1.209(2)
O(12)-C(59)	1.334(2)
O(12)-C(60)	1.459(2)
C(41)-C(46)	1.391(3)
C(41)-C(42)	1.400(3)
C(42)-C(43)	1.385(3)
C(42)-H(42)	0.9500
C(43)-C(44)	1.406(2)
C(43)-H(43)	0.9500
C(44)-C(45)	1.387(3)
C(44)-C(48)	1.473(2)
C(45)-C(46)	1.389(3)
C(45)-H(45)	0.9500
C(46)-H(46)	0.9500
C(47)-H(47A)	0.9800
C(47)-H(47B)	0.9800
C(47)-H(47C)	0.9800
C(48)-C(49)	1.318(3)
C(48)-H(48)	0.9500

C(49)-C(50)	1.527(2)
C(49)-H(49)	0.9500
C(50)-C(52)	1.523(3)
C(50)-C(51)	1.530(2)
C(50)-H(50)	1.0000
C(51)-H(51A)	0.9800
C(51)-H(51B)	0.9800
C(51)-H(51C)	0.9800
C(52)-C(53)	1.508(2)
C(53)-C(58)	1.394(3)
C(53)-C(54)	1.399(2)
C(54)-C(55)	1.390(3)
C(54)-H(54)	0.9500
C(55)-C(56)	1.398(3)
C(55)-H(55)	0.9500
C(56)-C(57)	1.393(3)
C(56)-C(59)	1.496(3)
C(57)-C(58)	1.380(3)
C(57)-H(57)	0.9500
C(58)-H(58)	0.9500
C(60)-H(60A)	0.9800
C(60)-H(60B)	0.9800
C(60)-H(60C)	0.9800

C(1)-O(1)-C(7)	116.87(14)
C(19)-O(4)-C(20)	115.65(13)
O(1)-C(1)-C(6)	124.50(16)
O(1)-C(1)-C(2)	115.68(16)
C(6)-C(1)-C(2)	119.82(17)
C(3)-C(2)-C(1)	120.26(17)
C(3)-C(2)-H(2)	119.9
C(1)-C(2)-H(2)	119.9
C(2)-C(3)-C(4)	121.12(17)
C(2)-C(3)-H(3)	119.4
C(4)-C(3)-H(3)	119.4
C(5)-C(4)-C(3)	117.21(17)
C(5)-C(4)-C(8)	120.03(16)
C(3)-C(4)-C(8)	122.65(16)

C(4)-C(5)-C(6)	122.66(17)
C(4)-C(5)-H(5)	118.7
C(6)-C(5)-H(5)	118.7
C(1)-C(6)-C(5)	118.94(17)
C(1)-C(6)-H(6)	120.5
C(5)-C(6)-H(6)	120.5
O(1)-C(7)-H(7A)	109.5
O(1)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
O(1)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
C(9)-C(8)-C(4)	127.58(16)
C(9)-C(8)-H(8)	116.2
C(4)-C(8)-H(8)	116.2
C(8)-C(9)-C(10)	122.97(16)
C(8)-C(9)-H(9)	118.5
C(10)-C(9)-H(9)	118.5
C(9)-C(10)-C(12)	110.11(15)
C(9)-C(10)-C(11)	111.83(15)
C(12)-C(10)-C(11)	110.02(14)
C(9)-C(10)-H(10)	108.3
C(12)-C(10)-H(10)	108.3
C(11)-C(10)-H(10)	108.3
C(10)-C(11)-H(11A)	109.5
C(10)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(10)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
O(2)-C(12)-C(13)	119.73(16)
O(2)-C(12)-C(10)	121.21(16)
C(13)-C(12)-C(10)	119.06(15)
C(14)-C(13)-C(18)	119.33(16)
C(14)-C(13)-C(12)	123.00(15)
C(18)-C(13)-C(12)	117.67(15)
C(15)-C(14)-C(13)	120.62(15)
C(15)-C(14)-H(14)	119.7

C(13)-C(14)-H(14) 119.7
C(14)-C(15)-C(16) 120.05(16)
C(14)-C(15)-H(15) 120.0
C(16)-C(15)-H(15) 120.0
C(17)-C(16)-C(15) 119.61(16)
C(17)-C(16)-C(19) 118.49(15)
C(15)-C(16)-C(19) 121.81(15)
C(18)-C(17)-C(16) 120.06(15)
C(18)-C(17)-H(17) 120.0
C(16)-C(17)-H(17) 120.0
C(17)-C(18)-C(13) 120.31(16)
C(17)-C(18)-H(18) 119.8
C(13)-C(18)-H(18) 119.8
O(3)-C(19)-O(4) 123.83(16)
O(3)-C(19)-C(16) 123.83(16)
O(4)-C(19)-C(16) 112.33(14)
O(4)-C(20)-H(20A) 109.5
O(4)-C(20)-H(20B) 109.5
H(20A)-C(20)-H(20B)109.5
O(4)-C(20)-H(20C) 109.5
H(20A)-C(20)-H(20C)109.5
H(20B)-C(20)-H(20C)109.5
C(21)-O(5)-C(27) 116.89(14)
C(39)-O(8)-C(40) 115.12(15)
O(5)-C(21)-C(22) 124.69(16)
O(5)-C(21)-C(26) 115.71(15)
C(22)-C(21)-C(26) 119.60(16)
C(21)-C(22)-C(23) 119.23(17)
C(21)-C(22)-H(22) 120.4
C(23)-C(22)-H(22) 120.4
C(22)-C(23)-C(24) 121.72(17)
C(22)-C(23)-H(23) 119.1
C(24)-C(23)-H(23) 119.1
C(25)-C(24)-C(23) 117.48(17)
C(25)-C(24)-C(28) 118.94(17)
C(23)-C(24)-C(28) 123.58(17)
C(26)-C(25)-C(24) 121.91(18)
C(26)-C(25)-H(25) 119.0

C(24)-C(25)-H(25) 119.0
C(25)-C(26)-C(21) 120.05(17)
C(25)-C(26)-H(26) 120.0
C(21)-C(26)-H(26) 120.0
O(5)-C(27)-H(27A) 109.5
O(5)-C(27)-H(27B) 109.5
H(27A)-C(27)-H(27B)109.5
O(5)-C(27)-H(27C) 109.5
H(27A)-C(27)-H(27C)109.5
H(27B)-C(27)-H(27C)109.5
C(29)-C(28)-C(24) 126.99(18)
C(29)-C(28)-H(28) 116.5
C(24)-C(28)-H(28) 116.5
C(28)-C(29)-C(30) 124.14(17)
C(28)-C(29)-H(29) 117.9
C(30)-C(29)-H(29) 117.9
C(31)-C(30)-C(32) 110.84(15)
C(31)-C(30)-C(29) 114.62(15)
C(32)-C(30)-C(29) 107.77(14)
C(31)-C(30)-H(30) 107.8
C(32)-C(30)-H(30) 107.8
C(29)-C(30)-H(30) 107.8
C(30)-C(31)-H(31A) 109.5
C(30)-C(31)-H(31B) 109.5
H(31A)-C(31)-H(31B)109.5
C(30)-C(31)-H(31C) 109.5
H(31A)-C(31)-H(31C)109.5
H(31B)-C(31)-H(31C)109.5
O(6)-C(32)-C(33) 119.23(16)
O(6)-C(32)-C(30) 121.05(16)
C(33)-C(32)-C(30) 119.69(15)
C(38)-C(33)-C(34) 119.23(16)
C(38)-C(33)-C(32) 123.68(15)
C(34)-C(33)-C(32) 117.07(15)
C(35)-C(34)-C(33) 120.62(16)
C(35)-C(34)-H(34) 119.7
C(33)-C(34)-H(34) 119.7
C(34)-C(35)-C(36) 120.00(16)

C(34)-C(35)-H(35) 120.0
C(36)-C(35)-H(35) 120.0
C(35)-C(36)-C(37) 119.87(16)
C(35)-C(36)-C(39) 117.94(16)
C(37)-C(36)-C(39) 122.12(16)
C(38)-C(37)-C(36) 120.20(16)
C(38)-C(37)-H(37) 119.9
C(36)-C(37)-H(37) 119.9
C(37)-C(38)-C(33) 120.08(16)
C(37)-C(38)-H(38) 120.0
C(33)-C(38)-H(38) 120.0
O(7)-C(39)-O(8) 123.63(17)
O(7)-C(39)-C(36) 123.99(16)
O(8)-C(39)-C(36) 112.35(15)
O(8)-C(40)-H(40A) 109.5
O(8)-C(40)-H(40B) 109.5
H(40A)-C(40)-H(40B)109.5
O(8)-C(40)-H(40C) 109.5
H(40A)-C(40)-H(40C)109.5
H(40B)-C(40)-H(40C)109.5
C(41)-O(9)-C(47) 117.37(15)
C(59)-O(12)-C(60) 115.00(15)
O(9)-C(41)-C(46) 124.67(16)
O(9)-C(41)-C(42) 115.78(16)
C(46)-C(41)-C(42) 119.55(16)
C(43)-C(42)-C(41) 120.12(17)
C(43)-C(42)-H(42) 119.9
C(41)-C(42)-H(42) 119.9
C(42)-C(43)-C(44) 121.24(17)
C(42)-C(43)-H(43) 119.4
C(44)-C(43)-H(43) 119.4
C(45)-C(44)-C(43) 117.22(16)
C(45)-C(44)-C(48) 119.67(16)
C(43)-C(44)-C(48) 123.09(16)
C(44)-C(45)-C(46) 122.63(17)
C(44)-C(45)-H(45) 118.7
C(46)-C(45)-H(45) 118.7
C(45)-C(46)-C(41) 119.23(17)

C(45)-C(46)-H(46) 120.4
C(41)-C(46)-H(46) 120.4
O(9)-C(47)-H(47A) 109.5
O(9)-C(47)-H(47B) 109.5
H(47A)-C(47)-H(47B)109.5
O(9)-C(47)-H(47C) 109.5
H(47A)-C(47)-H(47C)109.5
H(47B)-C(47)-H(47C)109.5
C(49)-C(48)-C(44) 127.98(17)
C(49)-C(48)-H(48) 116.0
C(44)-C(48)-H(48) 116.0
C(48)-C(49)-C(50) 123.17(17)
C(48)-C(49)-H(49) 118.4
C(50)-C(49)-H(49) 118.4
C(52)-C(50)-C(49) 106.75(14)
C(52)-C(50)-C(51) 111.32(15)
C(49)-C(50)-C(51) 113.07(15)
C(52)-C(50)-H(50) 108.5
C(49)-C(50)-H(50) 108.5
C(51)-C(50)-H(50) 108.5
C(50)-C(51)-H(51A) 109.5
C(50)-C(51)-H(51B) 109.5
H(51A)-C(51)-H(51B)109.5
C(50)-C(51)-H(51C) 109.5
H(51A)-C(51)-H(51C)109.5
H(51B)-C(51)-H(51C)109.5
O(10)-C(52)-C(53) 119.70(16)
O(10)-C(52)-C(50) 121.00(16)
C(53)-C(52)-C(50) 119.28(15)
C(58)-C(53)-C(54) 119.50(16)
C(58)-C(53)-C(52) 117.29(16)
C(54)-C(53)-C(52) 123.18(16)
C(55)-C(54)-C(53) 120.06(16)
C(55)-C(54)-H(54) 120.0
C(53)-C(54)-H(54) 120.0
C(54)-C(55)-C(56) 119.71(17)
C(54)-C(55)-H(55) 120.1
C(56)-C(55)-H(55) 120.1

C(57)-C(56)-C(55)	120.16(17)
C(57)-C(56)-C(59)	117.93(16)
C(55)-C(56)-C(59)	121.91(17)
C(58)-C(57)-C(56)	119.84(16)
C(58)-C(57)-H(57)	120.1
C(56)-C(57)-H(57)	120.1
C(57)-C(58)-C(53)	120.66(17)
C(57)-C(58)-H(58)	119.7
C(53)-C(58)-H(58)	119.7
O(11)-C(59)-O(12)	124.15(18)
O(11)-C(59)-C(56)	123.60(17)
O(12)-C(59)-C(56)	112.25(15)
O(12)-C(60)-H(60A)	109.5
O(12)-C(60)-H(60B)	109.5
H(60A)-C(60)-H(60B)	109.5
O(12)-C(60)-H(60C)	109.5
H(60A)-C(60)-H(60C)	109.5
H(60B)-C(60)-H(60C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for d09054. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	32(1)	34(1)	30(1)	-2(1)	4(1)	0(1)
O(2)	26(1)	27(1)	41(1)	1(1)	4(1)	3(1)
O(3)	36(1)	21(1)	44(1)	3(1)	10(1)	-3(1)
O(4)	29(1)	23(1)	36(1)	4(1)	9(1)	3(1)
C(1)	28(1)	23(1)	30(1)	2(1)	2(1)	5(1)
C(2)	30(1)	23(1)	34(1)	-3(1)	-4(1)	2(1)
C(3)	26(1)	23(1)	36(1)	5(1)	0(1)	-2(1)
C(4)	25(1)	18(1)	31(1)	5(1)	-1(1)	3(1)
C(5)	28(1)	23(1)	30(1)	1(1)	-2(1)	0(1)
C(6)	25(1)	25(1)	34(1)	4(1)	2(1)	1(1)
C(7)	36(1)	40(1)	32(1)	1(1)	5(1)	2(1)
C(8)	30(1)	17(1)	32(1)	4(1)	-3(1)	0(1)
C(9)	29(1)	19(1)	30(1)	2(1)	-2(1)	2(1)
C(10)	27(1)	23(1)	30(1)	1(1)	0(1)	0(1)
C(11)	39(1)	22(1)	46(1)	-1(1)	7(1)	-1(1)
C(12)	27(1)	24(1)	22(1)	0(1)	-1(1)	0(1)
C(13)	24(1)	24(1)	21(1)	1(1)	-1(1)	-1(1)
C(14)	25(1)	22(1)	26(1)	4(1)	4(1)	-2(1)
C(15)	24(1)	25(1)	24(1)	0(1)	4(1)	0(1)
C(16)	26(1)	22(1)	18(1)	-1(1)	0(1)	-2(1)
C(17)	27(1)	23(1)	23(1)	0(1)	3(1)	-4(1)
C(18)	22(1)	25(1)	25(1)	-2(1)	2(1)	-2(1)
C(19)	26(1)	23(1)	21(1)	-2(1)	-1(1)	-2(1)
C(20)	32(1)	21(1)	36(1)	2(1)	4(1)	5(1)
O(5)	31(1)	26(1)	27(1)	1(1)	6(1)	0(1)
O(6)	27(1)	30(1)	46(1)	1(1)	1(1)	2(1)
O(7)	39(1)	23(1)	44(1)	0(1)	3(1)	-4(1)
O(8)	33(1)	22(1)	54(1)	0(1)	10(1)	4(1)
C(21)	27(1)	21(1)	27(1)	-2(1)	4(1)	-7(1)
C(22)	27(1)	27(1)	34(1)	0(1)	3(1)	-1(1)
C(23)	39(1)	28(1)	28(1)	4(1)	-2(1)	-5(1)
C(24)	30(1)	25(1)	34(1)	-4(1)	6(1)	-5(1)

C(25)29(1)	25(1)	37(1)	-3(1)	5(1)	-2(1)
C(26)31(1)	24(1)	32(1)	1(1)	1(1)	-4(1)
C(27)31(1)	44(1)	30(1)	-4(1)	9(1)	-1(1)
C(28)30(1)	28(1)	35(1)	-2(1)	-1(1)	2(1)
C(29)33(1)	25(1)	34(1)	-2(1)	7(1)	0(1)
C(30)30(1)	21(1)	25(1)	0(1)	4(1)	-1(1)
C(31)36(1)	24(1)	32(1)	-1(1)	5(1)	2(1)
C(32)26(1)	26(1)	21(1)	0(1)	0(1)	2(1)
C(33)27(1)	23(1)	18(1)	0(1)	4(1)	-2(1)
C(34)22(1)	28(1)	25(1)	0(1)	2(1)	-1(1)
C(35)30(1)	25(1)	26(1)	-2(1)	3(1)	-6(1)
C(36)28(1)	24(1)	23(1)	-1(1)	5(1)	-1(1)
C(37)24(1)	28(1)	24(1)	0(1)	4(1)	1(1)
C(38)26(1)	22(1)	23(1)	-1(1)	4(1)	-2(1)
C(39)30(1)	26(1)	26(1)	-1(1)	5(1)	0(1)
C(40)42(1)	24(1)	63(1)	4(1)	16(1)	9(1)
O(9) 41(1)	40(1)	27(1)	-3(1)	6(1)	-12(1)
O(10)42(1)	26(1)	32(1)	-2(1)	1(1)	-3(1)
O(11)34(1)	33(1)	47(1)	1(1)	-4(1)	4(1)
O(12)43(1)	21(1)	51(1)	-3(1)	-6(1)	2(1)
C(41)30(1)	25(1)	25(1)	3(1)	2(1)	2(1)
C(42)36(1)	30(1)	26(1)	-2(1)	-3(1)	-5(1)
C(43)28(1)	25(1)	32(1)	4(1)	2(1)	-5(1)
C(44)26(1)	21(1)	27(1)	3(1)	1(1)	3(1)
C(45)32(1)	25(1)	24(1)	1(1)	0(1)	0(1)
C(46)28(1)	26(1)	28(1)	3(1)	1(1)	-4(1)
C(47)41(1)	62(2)	28(1)	-2(1)	9(1)	-17(1)
C(48)32(1)	24(1)	28(1)	0(1)	0(1)	-1(1)
C(49)31(1)	23(1)	28(1)	0(1)	1(1)	0(1)
C(50)28(1)	22(1)	30(1)	2(1)	5(1)	0(1)
C(51)38(1)	31(1)	35(1)	4(1)	9(1)	7(1)
C(52)31(1)	24(1)	23(1)	1(1)	9(1)	-4(1)
C(53)28(1)	25(1)	21(1)	2(1)	6(1)	-1(1)
C(54)26(1)	29(1)	28(1)	0(1)	2(1)	0(1)
C(55)32(1)	25(1)	34(1)	-4(1)	2(1)	-2(1)
C(56)29(1)	26(1)	25(1)	1(1)	5(1)	3(1)
C(57)28(1)	30(1)	22(1)	1(1)	2(1)	-2(1)
C(58)31(1)	26(1)	23(1)	0(1)	8(1)	-2(1)

C(59)33(1)	28(1)	29(1)	-2(1)	1(1)	1(1)
C(60)52(1)	23(1)	58(1)	-2(1)	-6(1)	5(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for d09054.

	x	y	z	U(eq)
H(2)	10053	7593	9720	35
H(3)	11376	7550	8529	34
H(5)	6210	6532	7867	32
H(6)	4897	6554	9064	33
H(7A)	3459	7007	10051	54
H(7B)	4301	6967	10912	54
H(7C)	4779	6453	10354	54
H(8)	8475	6958	6909	32
H(9)	12839	7168	7416	31
H(10)	10709	7175	5930	32
H(11A)	14643	6512	6288	53
H(11B)	13573	6599	5458	53
H(11C)	12243	6250	6058	53
H(14)	9674	8054	6499	29
H(15)	8291	8984	6457	29
H(17)	13916	9522	5517	29
H(18)	15335	8592	5592	29
H(20A)	7802	10835	6269	44
H(20B)	5433	10524	6172	44
H(20C)	6884	10621	5461	44
H(22)	-1200	9175	10881	35
H(23)	352	9167	9714	38
H(25)	5358	8161	10535	36
H(26)	3845	8157	11693	35
H(27A)	-1382	9359	12154	52
H(27B)	-1969	8887	12759	52
H(27C)	-2760	8800	11899	52
H(28)	5381	8417	9250	37
H(29)	2191	9170	8679	37
H(30)	3492	8941	7514	30
H(31A)	7134	8303	8180	46

H(31B)	6393	8323	7309	46
H(31C)	4843	8013	7883	46
H(34)	8307	10369	8146	30
H(35)	7131	11314	8012	32
H(37)	948	10768	7333	30
H(38)	2105	9819	7486	28
H(40A)	500	12534	8076	64
H(40B)	-1411	12393	7446	64
H(40C)	952	12627	7213	64
H(42)	5601	9874	-88	37
H(43)	3864	9797	1034	34
H(45)	8390	10877	2006	32
H(46)	10130	10969	886	33
H(47A)	10407	11193	-405	65
H(47B)	11427	10742	-964	65
H(47C)	12032	10698	-86	65
H(48)	5589	10512	2766	33
H(49)	2685	9688	2190	33
H(50)	1455	9574	3376	32
H(51A)	737	10410	4065	52
H(51B)	-46	10504	3206	52
H(51C)	2240	10779	3535	52
H(54)	2876	8751	3461	33
H(55)	4421	7846	3694	36
H(57)	10021	8589	4624	32
H(58)	8399	9486	4450	32
H(60A)	9267	6508	4146	67
H(60B)	6809	6274	4263	67
H(60C)	8264	6539	4953	67

Table 1, entry 1

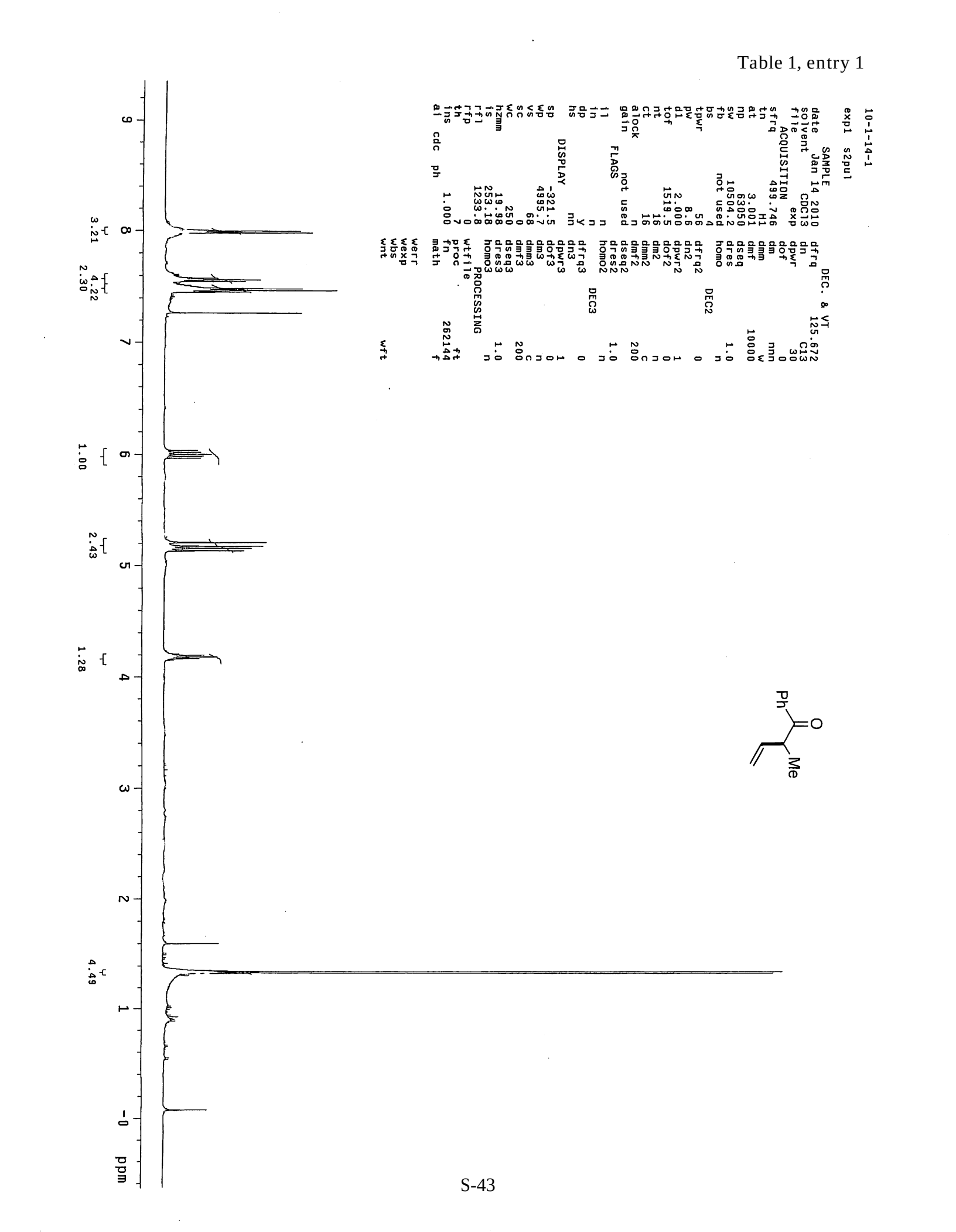


Table 1, entry 2

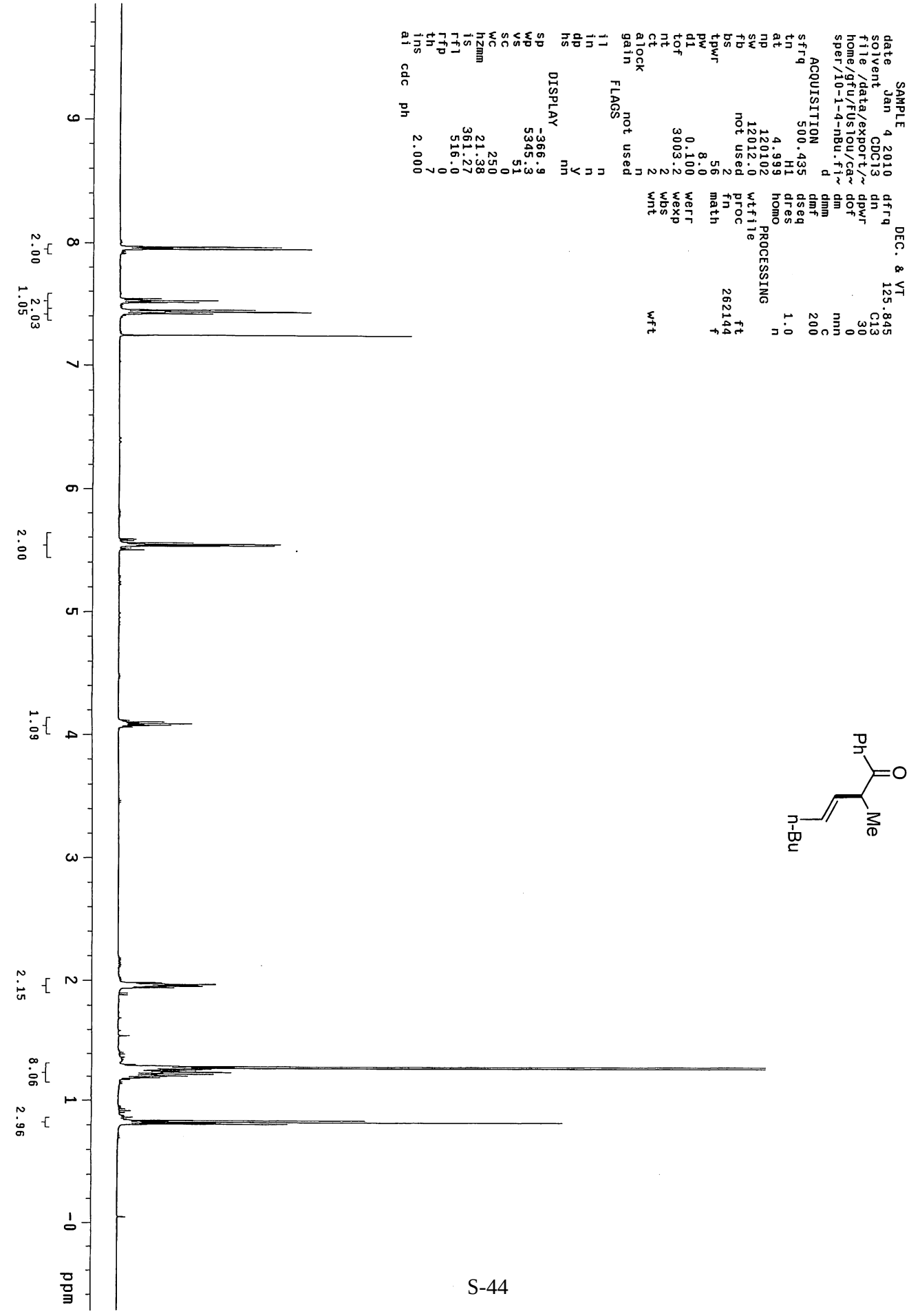


Table 1, entry 3

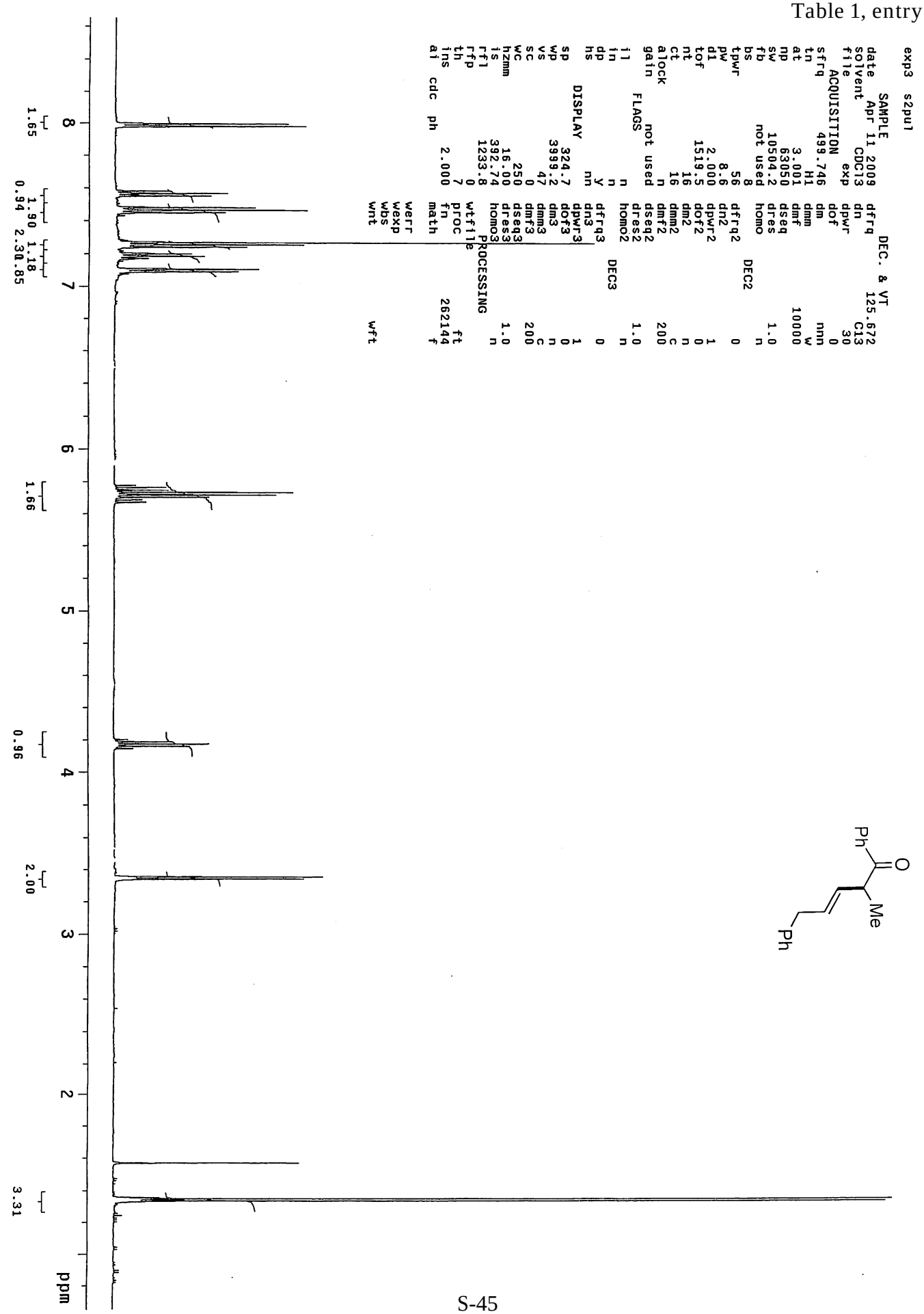


Table 1, entry 4

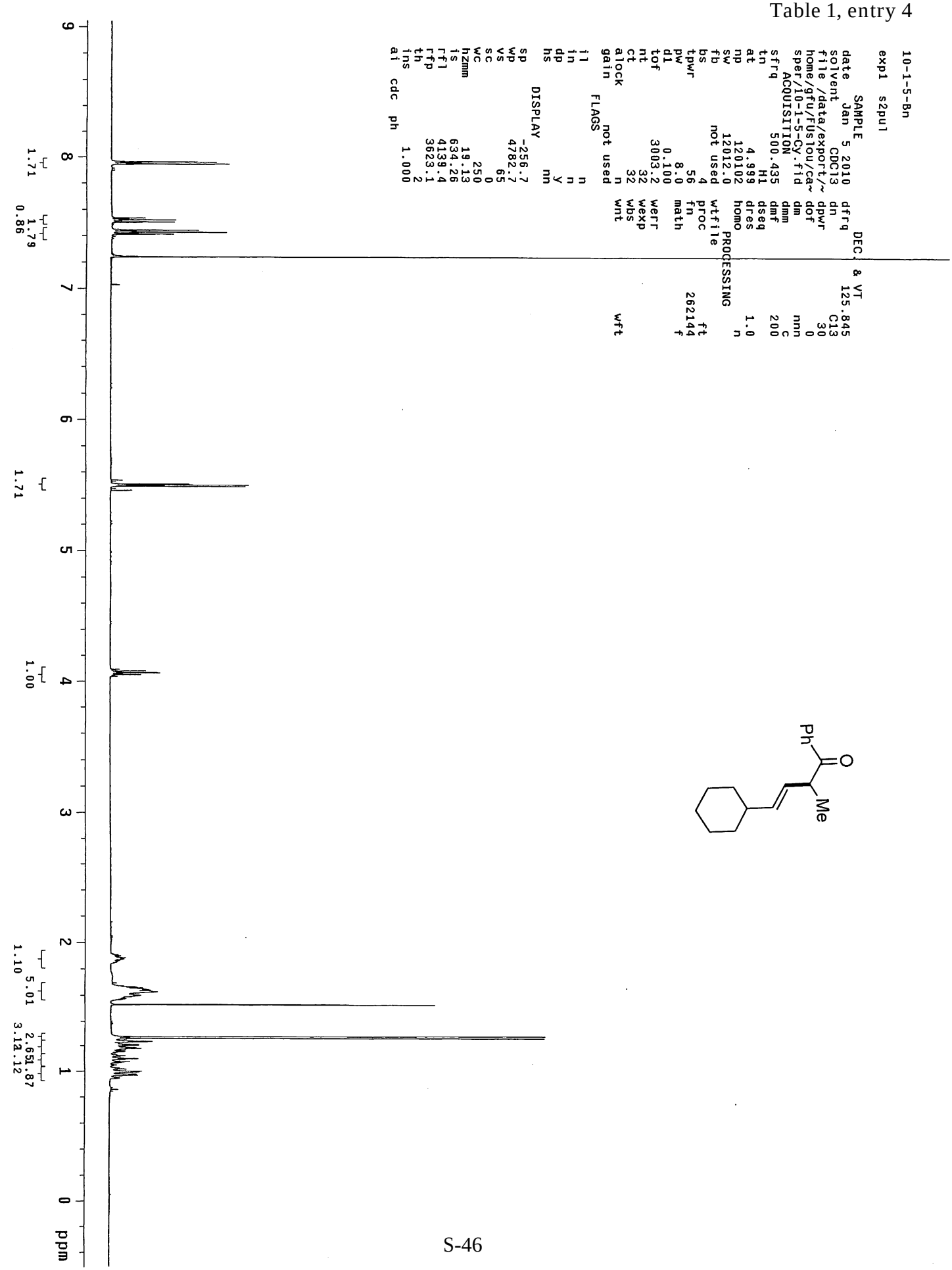


Table 1, entry 5

10-2-19-3

exp1 s2pul

SAMPLE		DEC. & VT	
date	Feb 19 2010	dfrq	125.794
solvent	CDCl3	dn	C13
file	exp	dpwr	38
ACQUISITION		dof	0
sfrq	500.231	dm	nnn
tn	H1	dmm	c
at	3.200	dmf	10000
np	64000	dseq	
sw	10000.0	dres	1.0
fb	not used	homo	n
bs	4	PROCESSING	
ss	1	wtfile	
tpwr	58	proc	ft
pw	9.0	fn	131072
d1	0	math	f
tof	1498.2		
nt	16	werr	
ct	16	wexp	
alock	n	wbs	
gain	not used	wnt	
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-274.3		
wp	4722.8		
vs	151		
sc	0		
wc	250		
hzmm	18.89		
is	427.66		
rfl	4633.9		
rfp	3631.7		
th	7		
ins	1.000		
nm	ph		

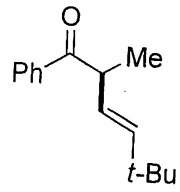


Table 1, entry 6

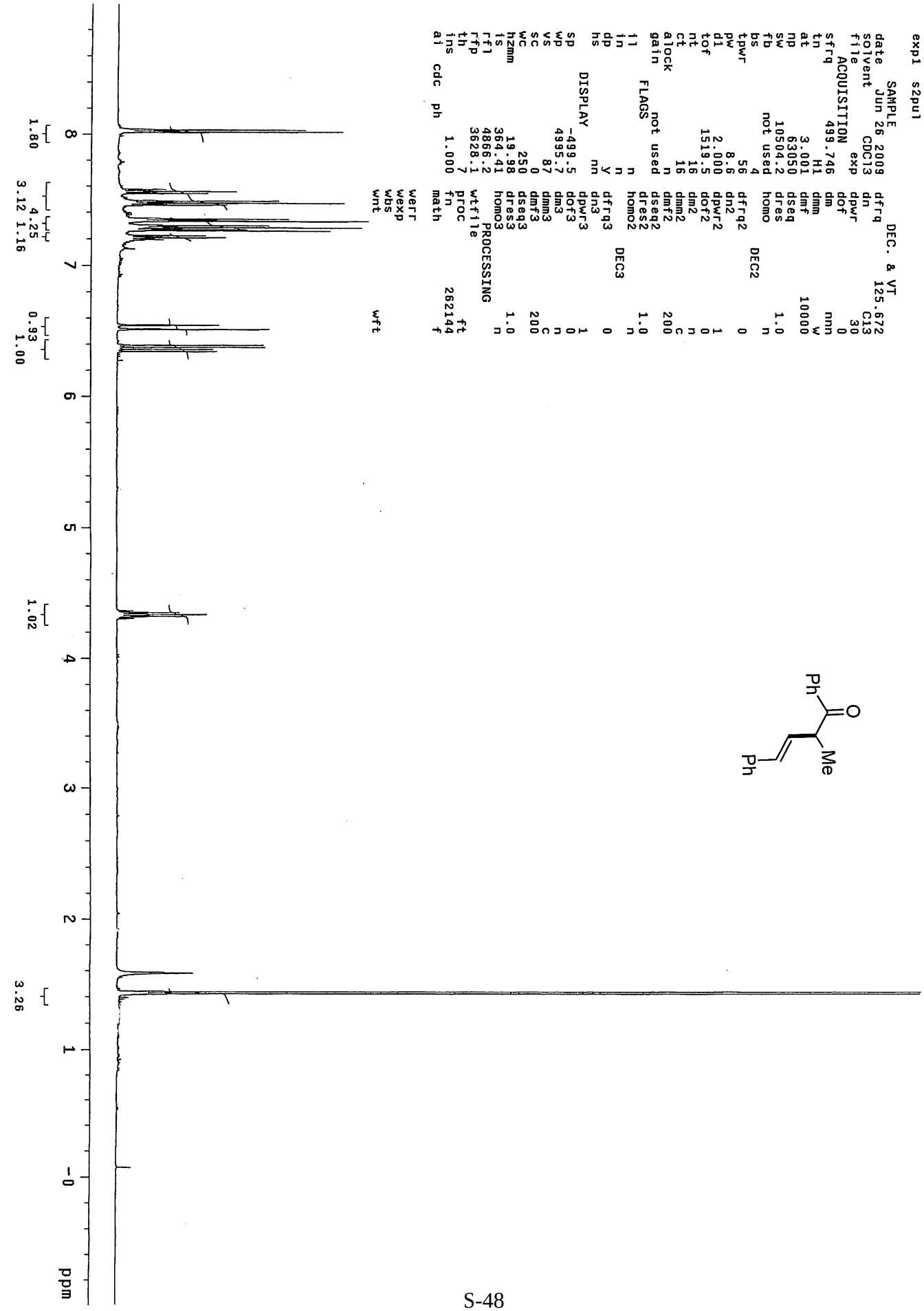


Table 1, entry 7

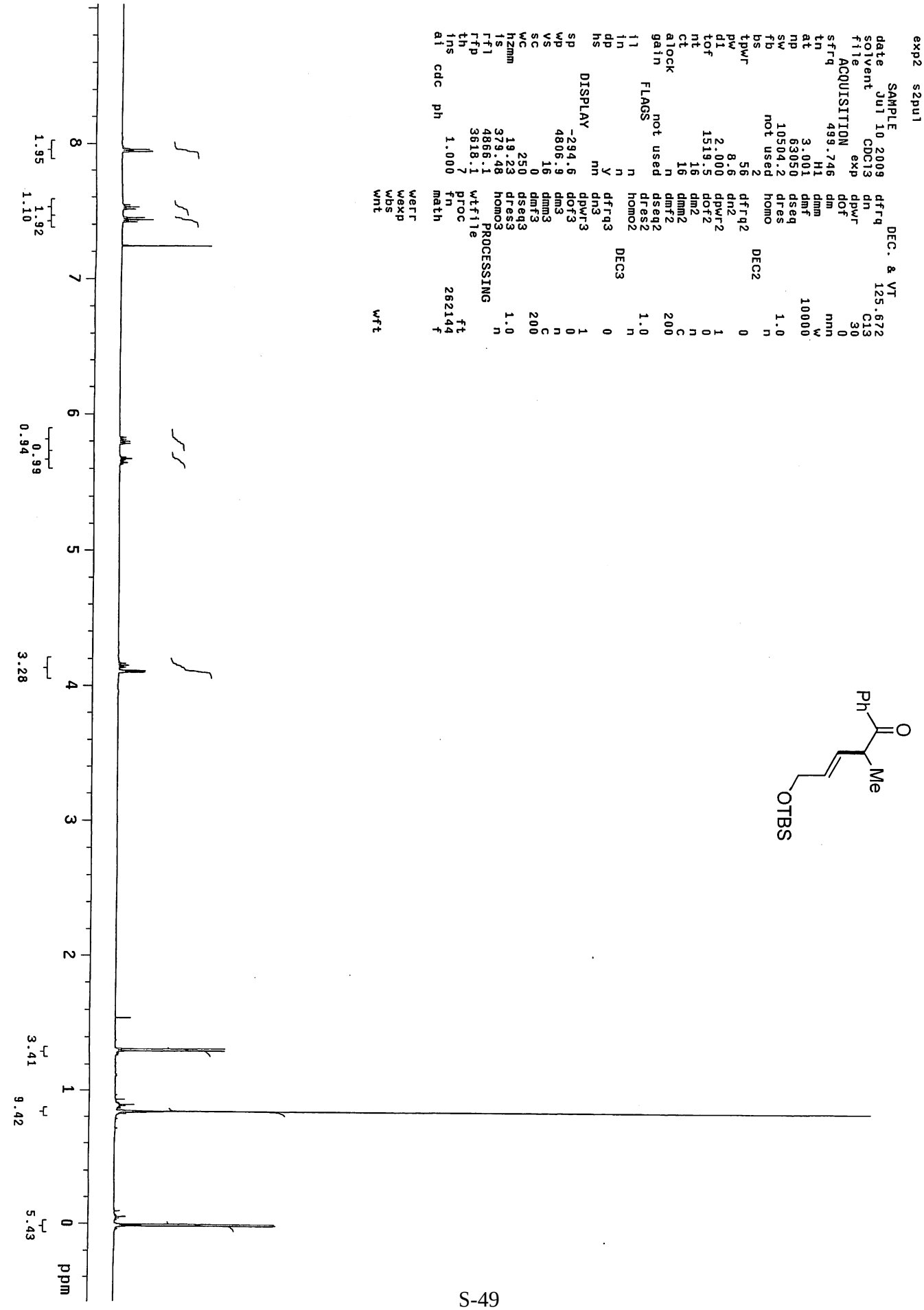


Table 1, entry 8

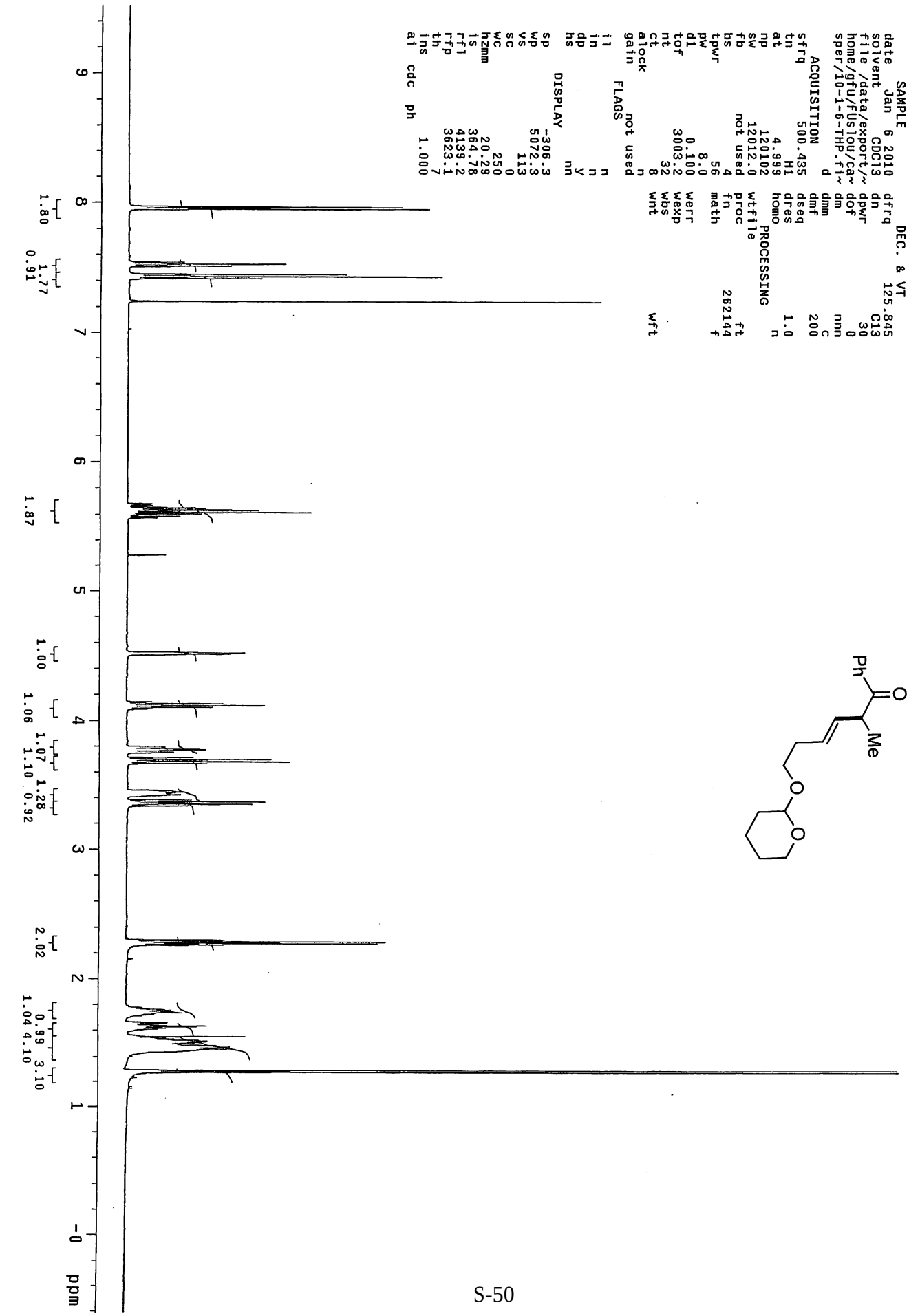


Table 1, entry 9

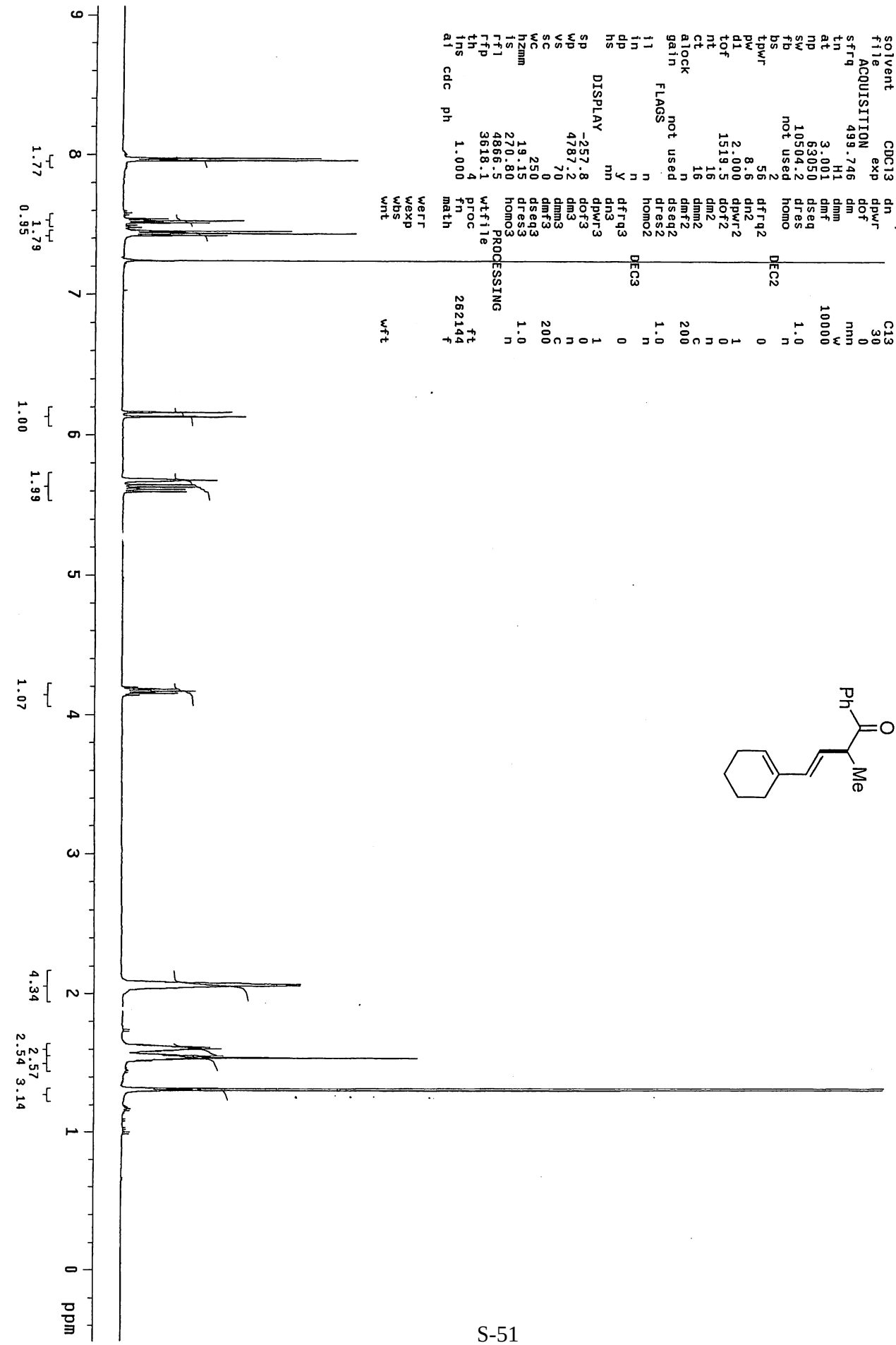


Table 2, entry 1

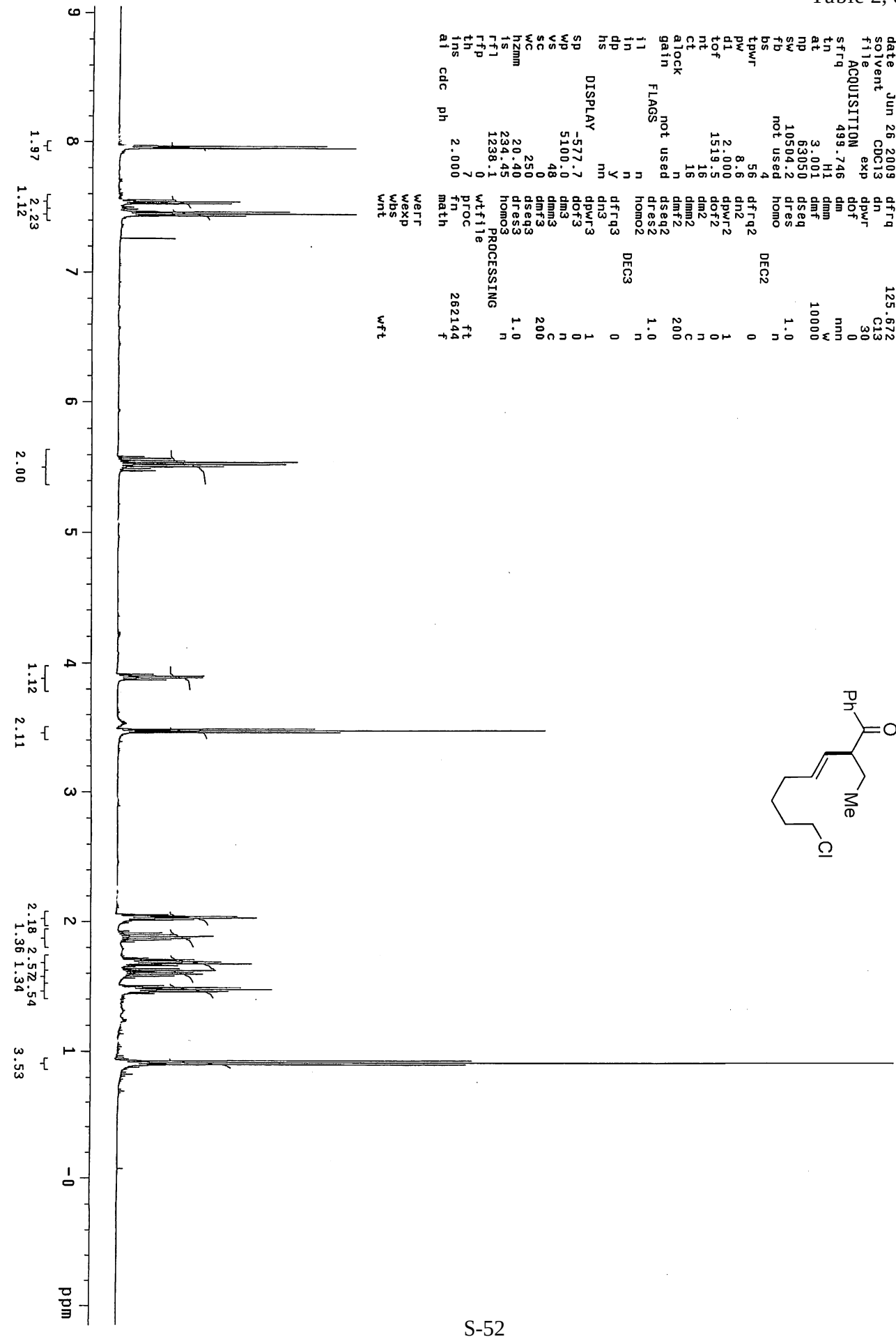


Table 2, entry 2

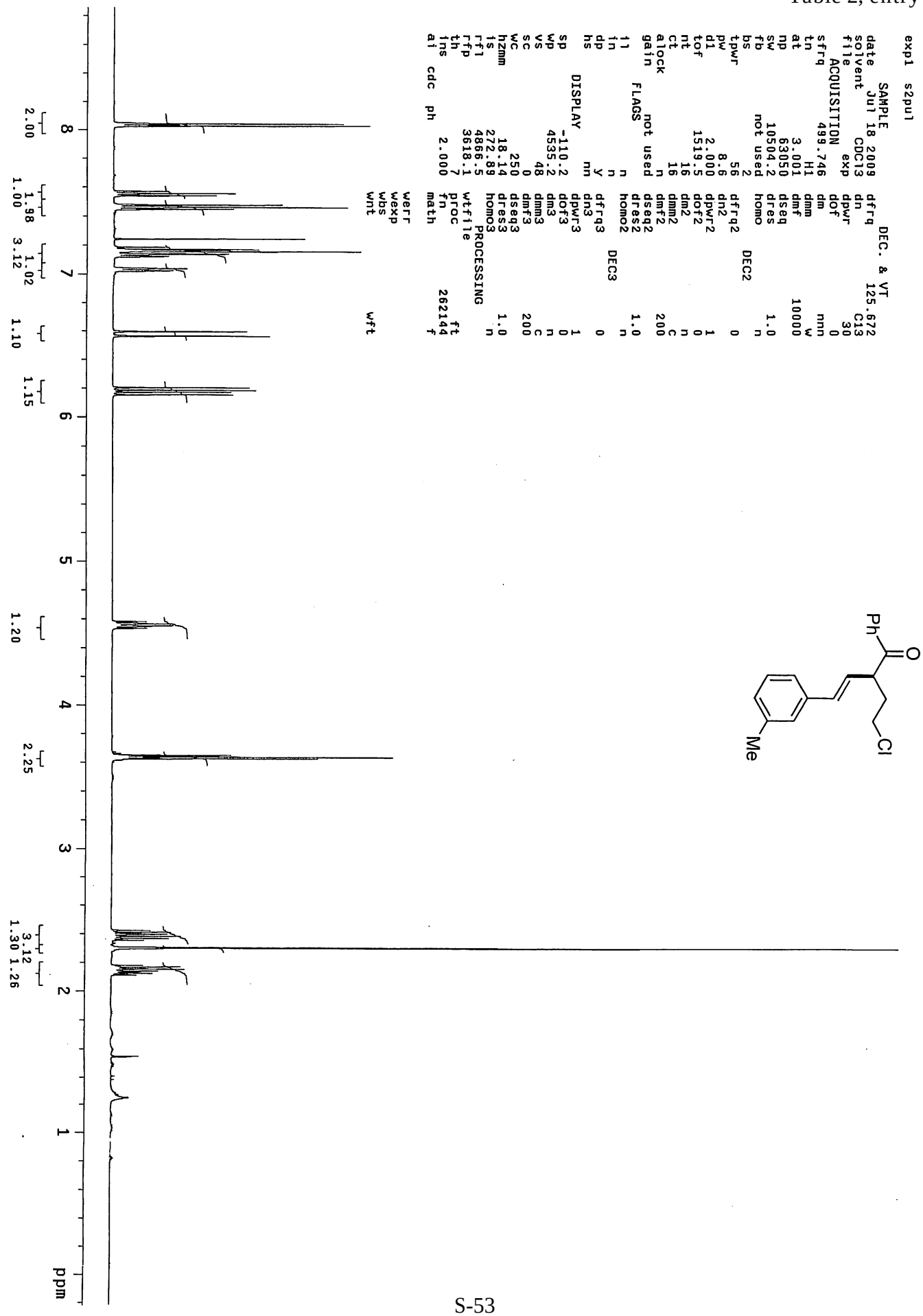


Table 2, entry 3

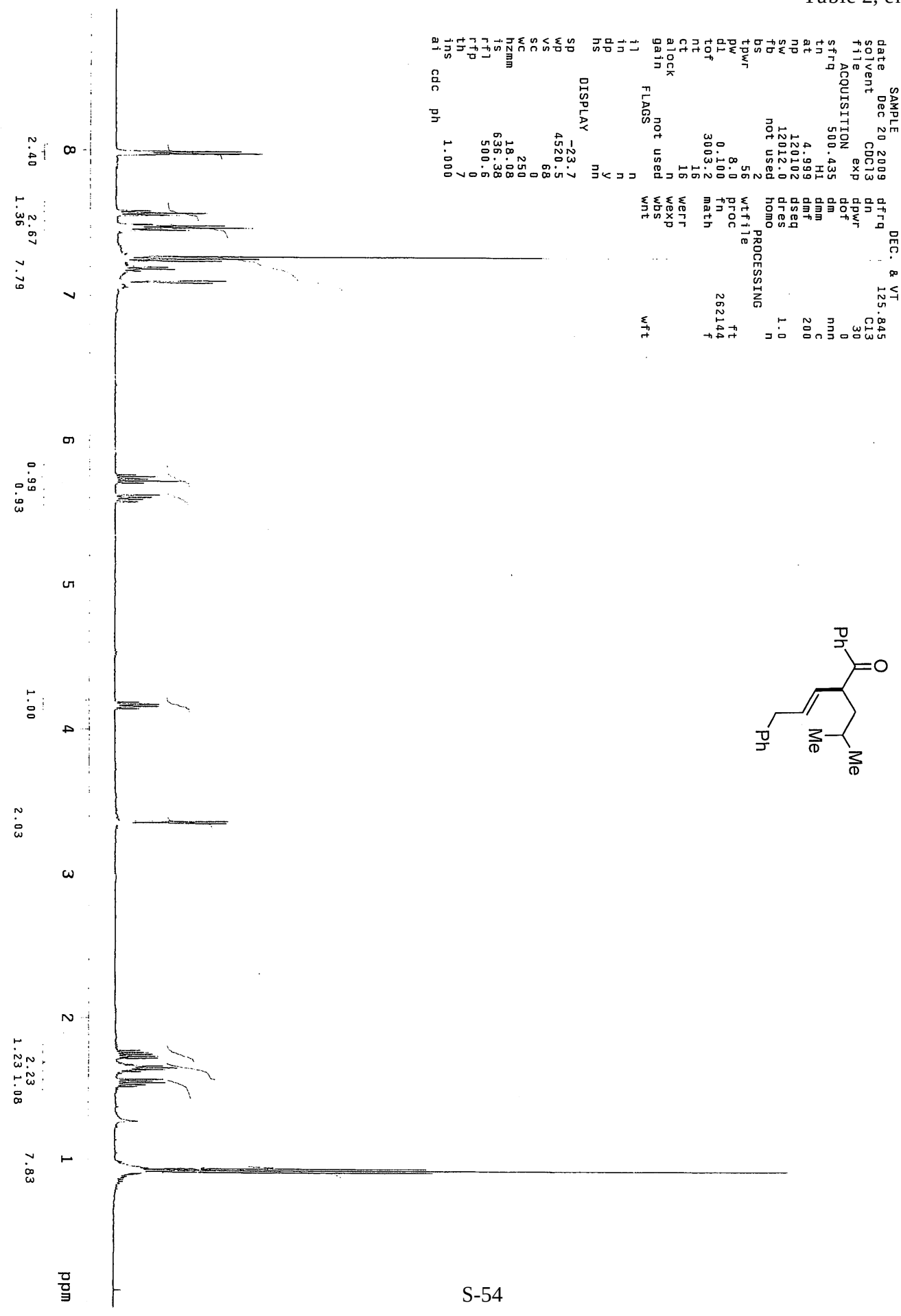


Table 2, entry 4

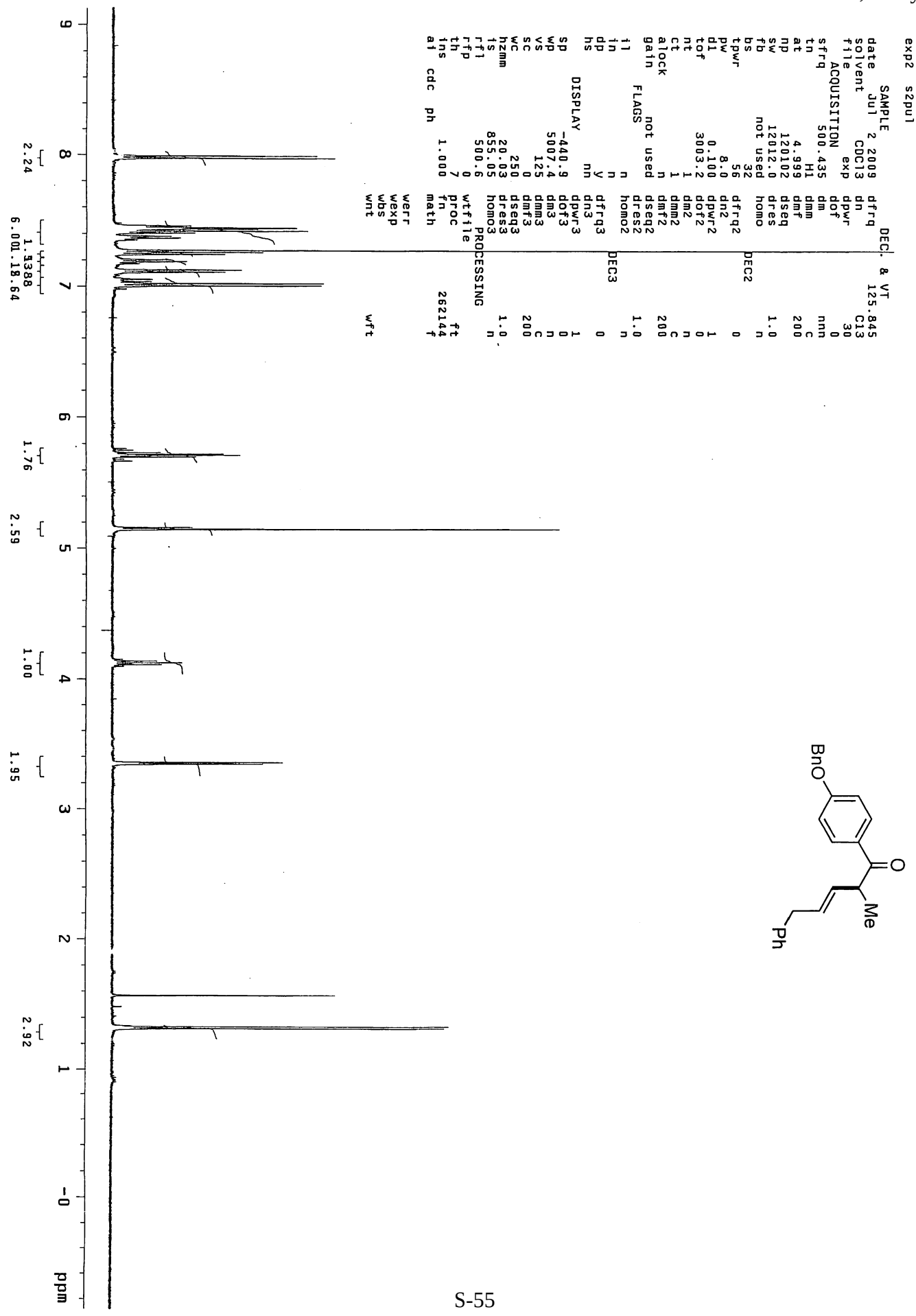
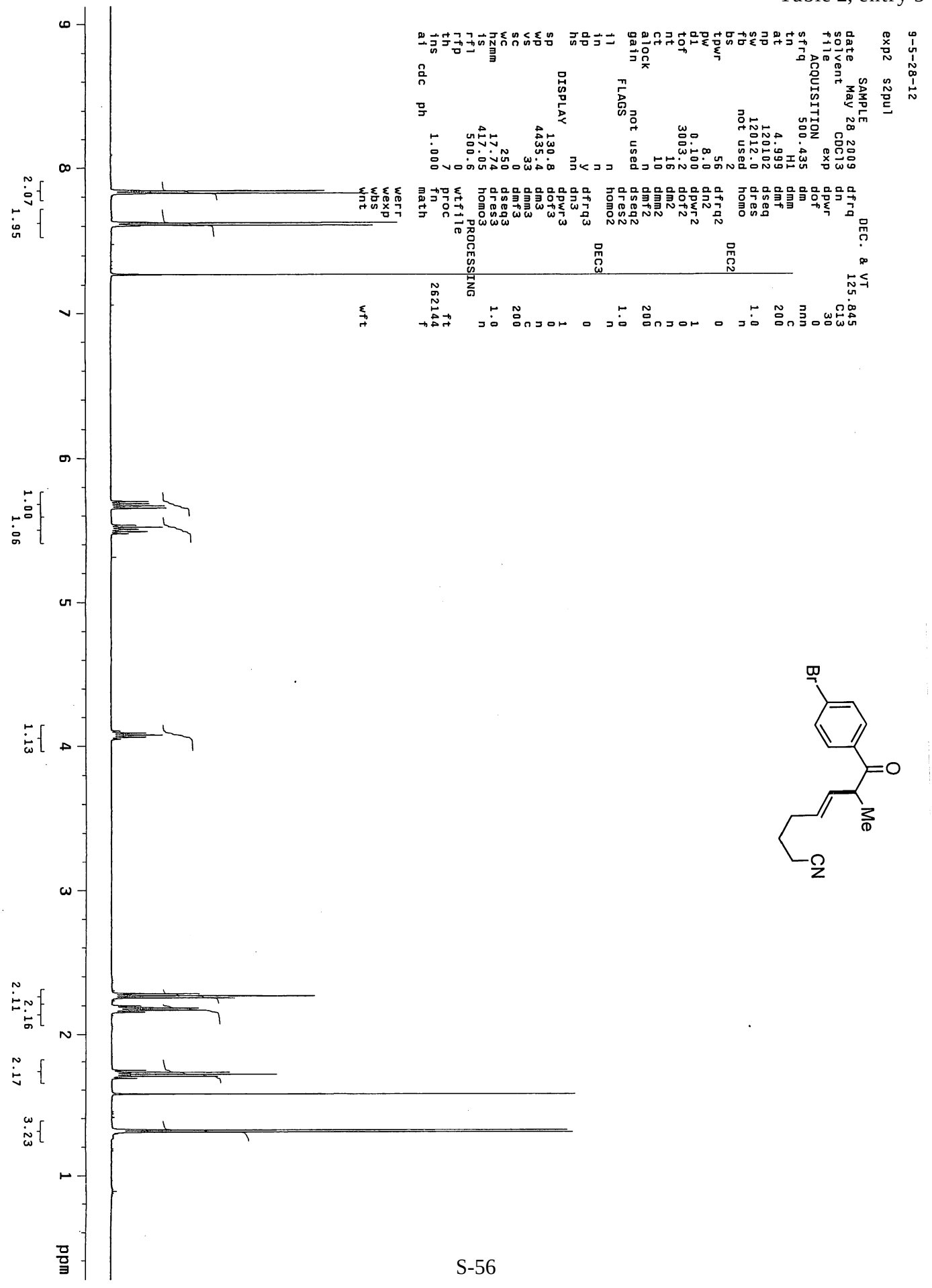


Table 2, entry 5



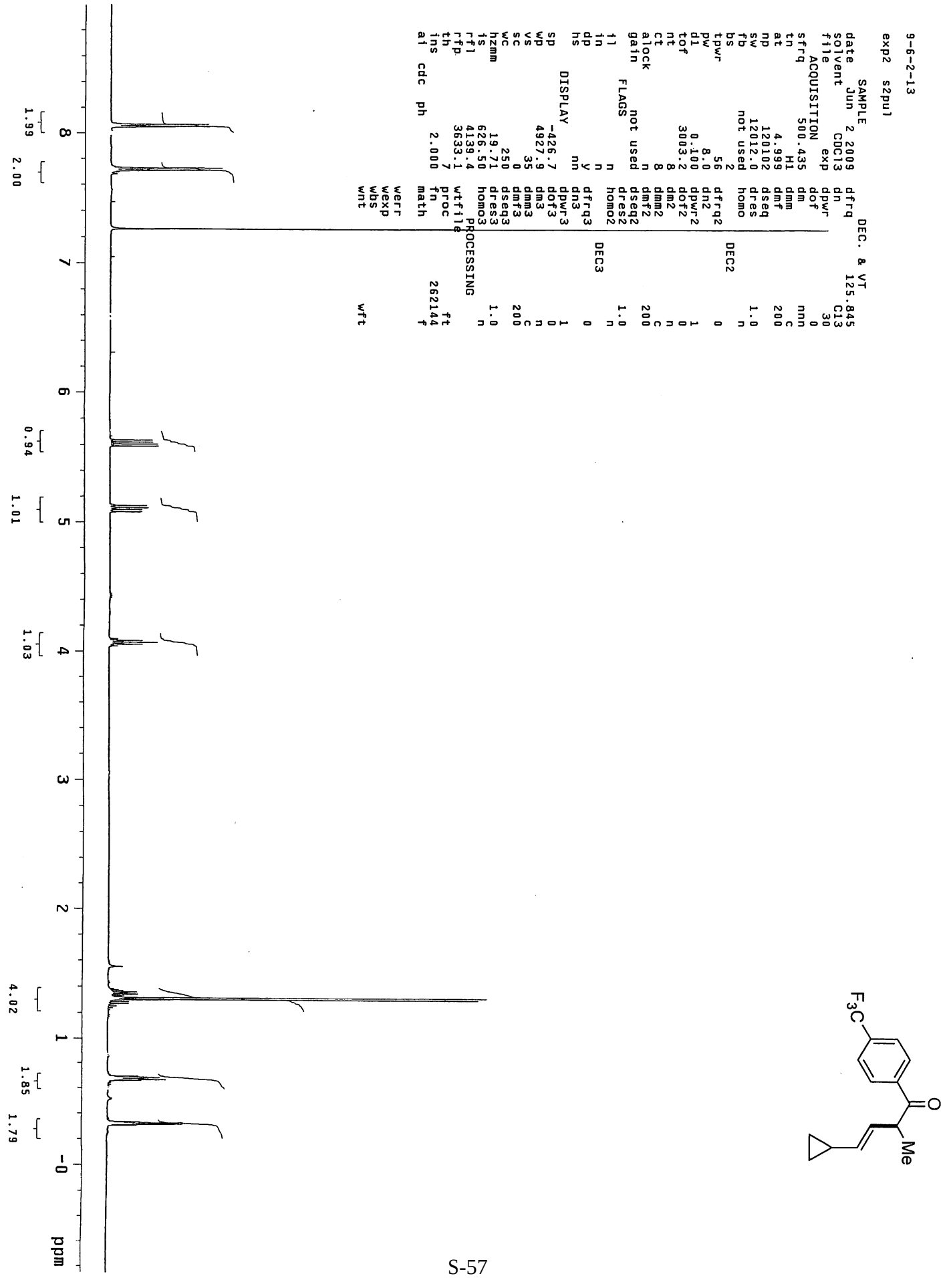

9-6-2-13
exp2 s2pul
SAMPLE
date Jun 2 2009
solvent CDCl3
file
ACQUISITION
sfrq 500.435
tn H1
at 4.999
np 120102
sw 12012.0
fb not used
bs 2
tpwr 56
pw 8.0
d1 0.100
tof 3003.2
nt 8
ct 8
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -426.7
wp 4927.9
vs 35
sc 0
wc 250
hzmm 19.71
is 626.50
rfl 4139.4
rfp 3633.1
th 7
ins 2.000
ai cdc ph
werr
wexp
wbs
wnt
dfrq DEC. & VT
dn 125.845
dof C13
dpwr 30
dm 0
dmm nnn
dmf c
dseq 200
dres
homo
DEC2
dfrq2
dn2 0
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 200
dseq2
dres2 1.0
homo2 n
DEC3
dfrq3
dn3
dpwr3 1
dof3 0
dm3 n
dmm3 c
dmf3 200
dseq3
dres3 1.0
homo3 n
PROCESSING
wtfile
proc ft
fn 262144
math f
wft
F3C
O
Me
1.99
2.00
0.94
1.01
1.03
4.02
1.85
1.79
8
7
6
5
4
3
2
1
-0
ppm

Table 2, entry 7

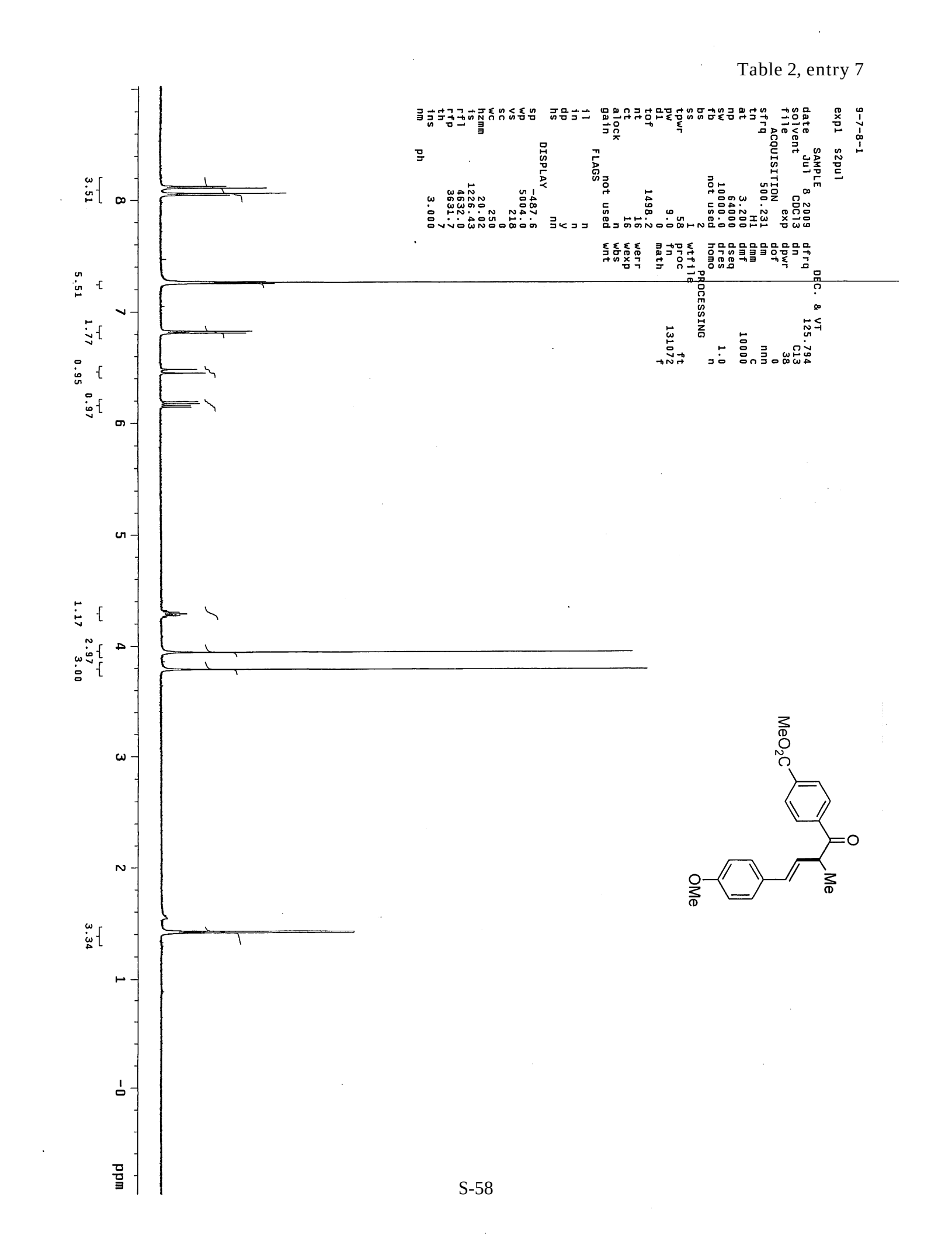


Table 2, entry 8

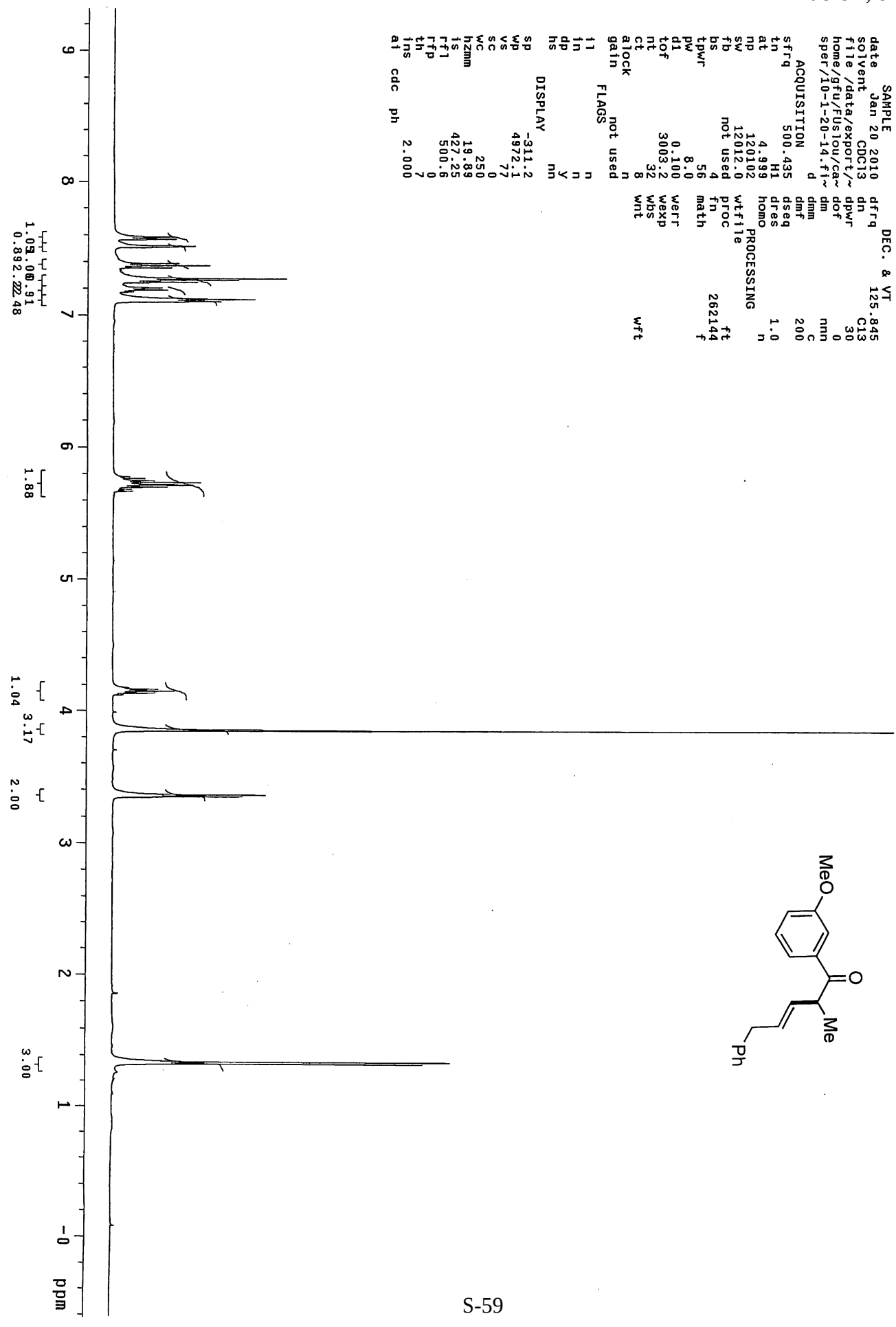


Table 2, entry 9

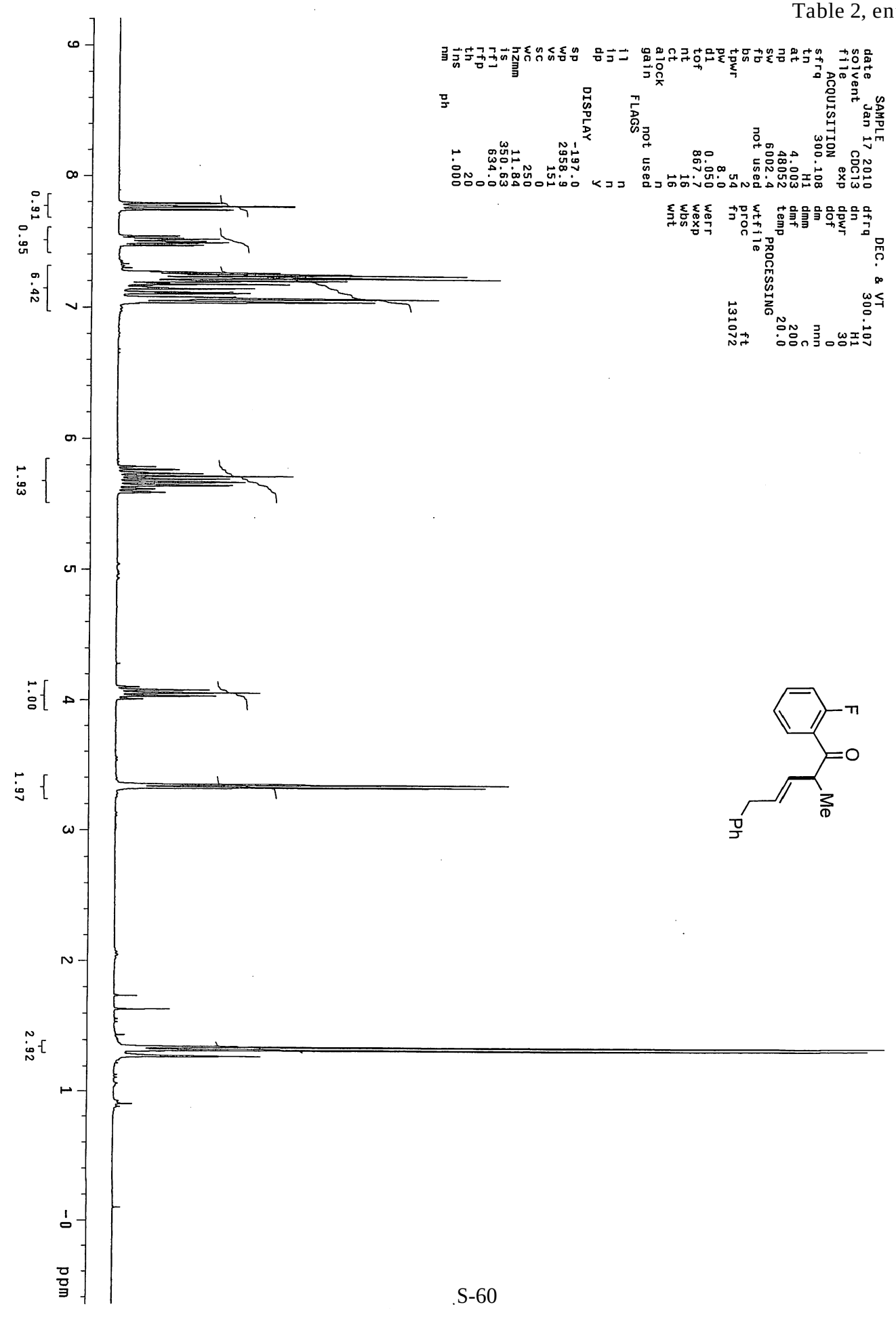


Table 2, entry 10

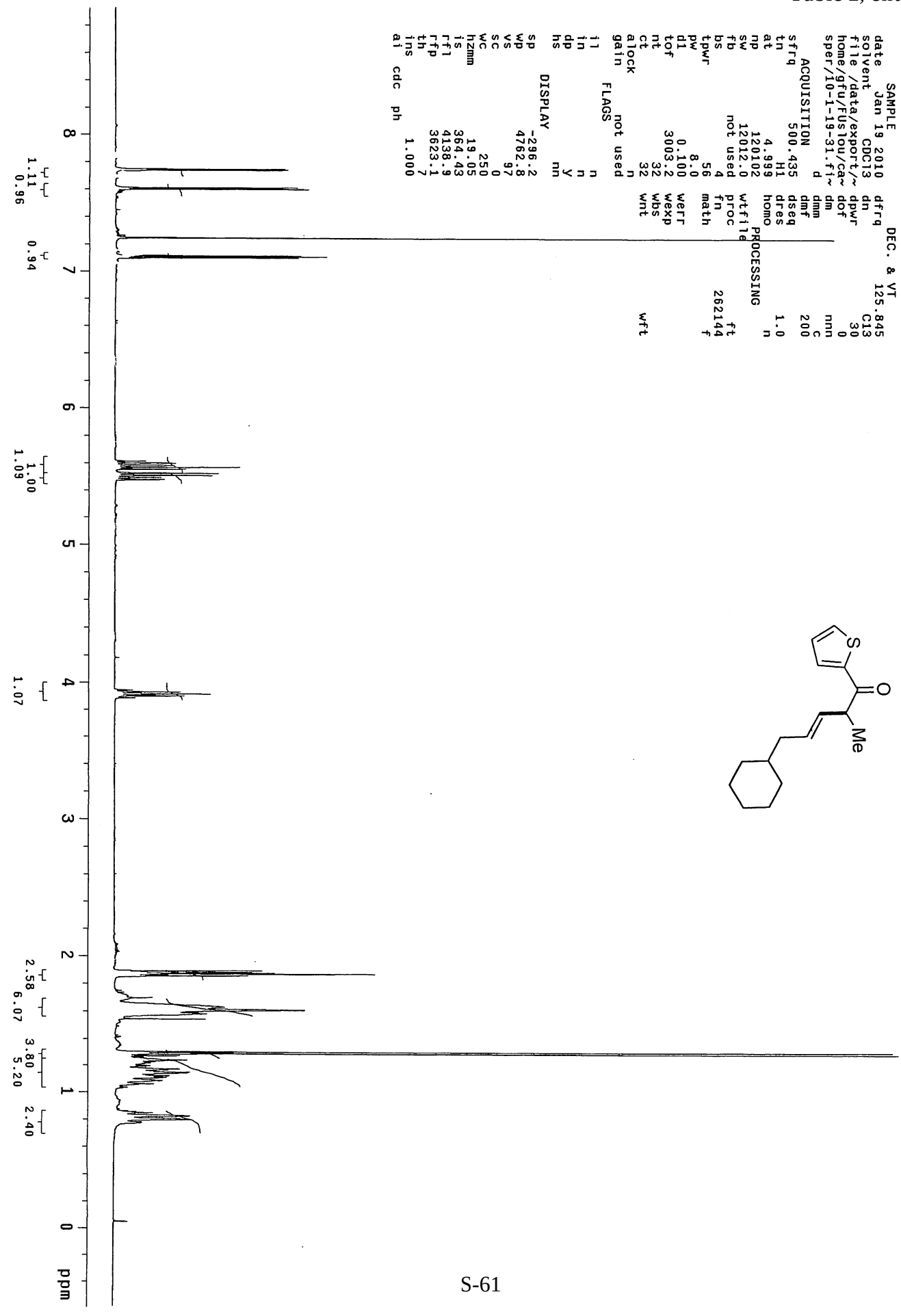


Table 3, entry 1

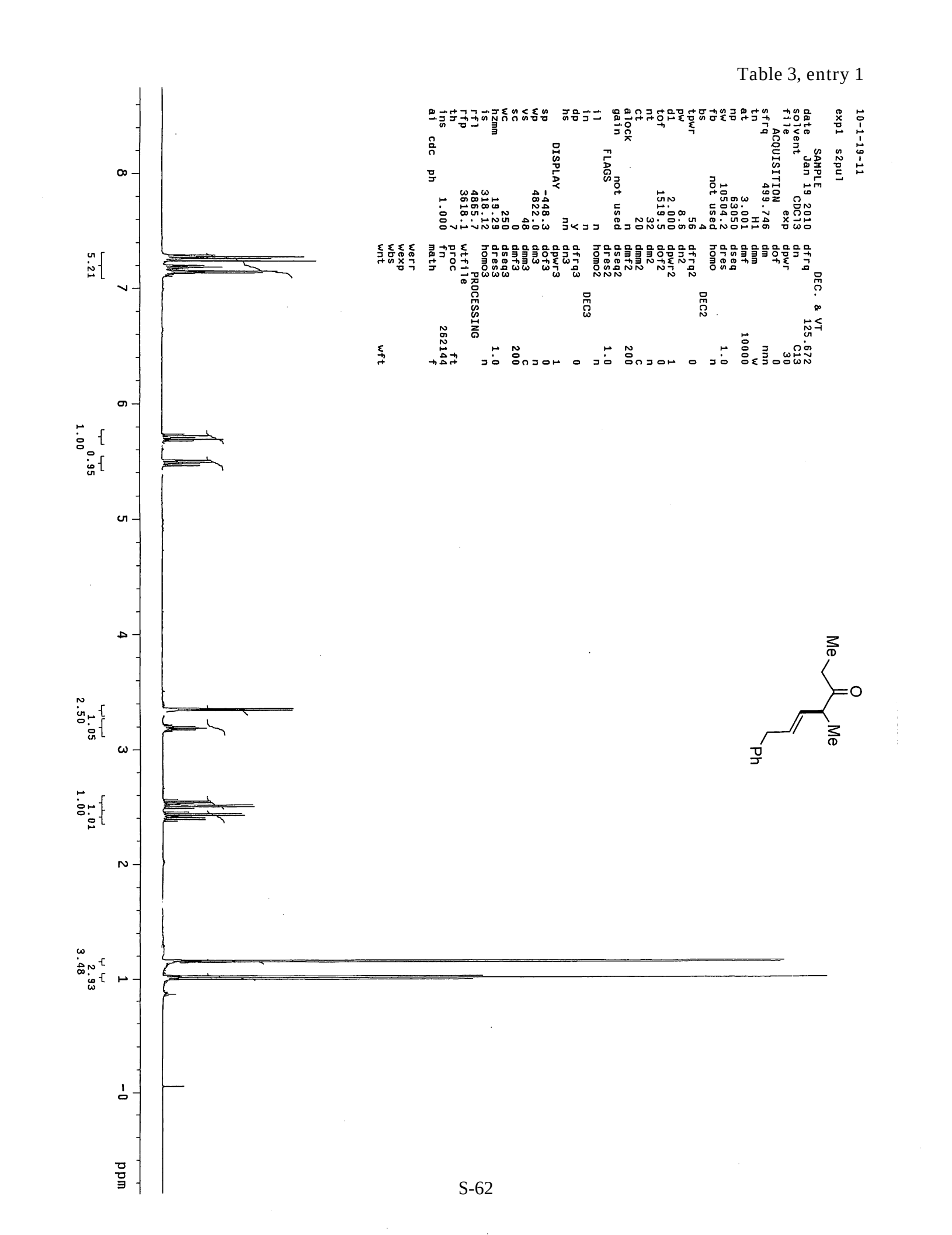


Table 3, entry 2

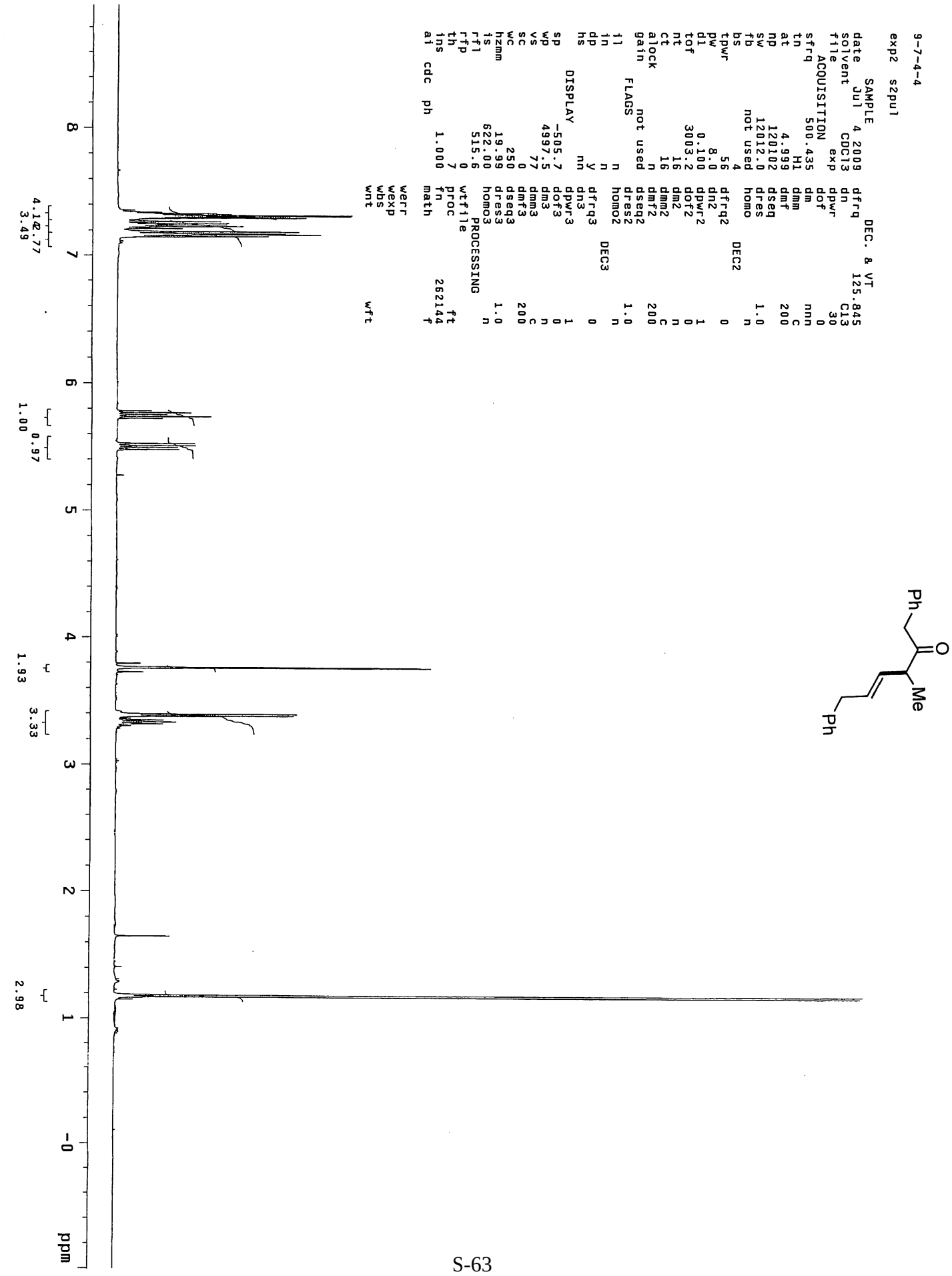


Table 3, entry 3

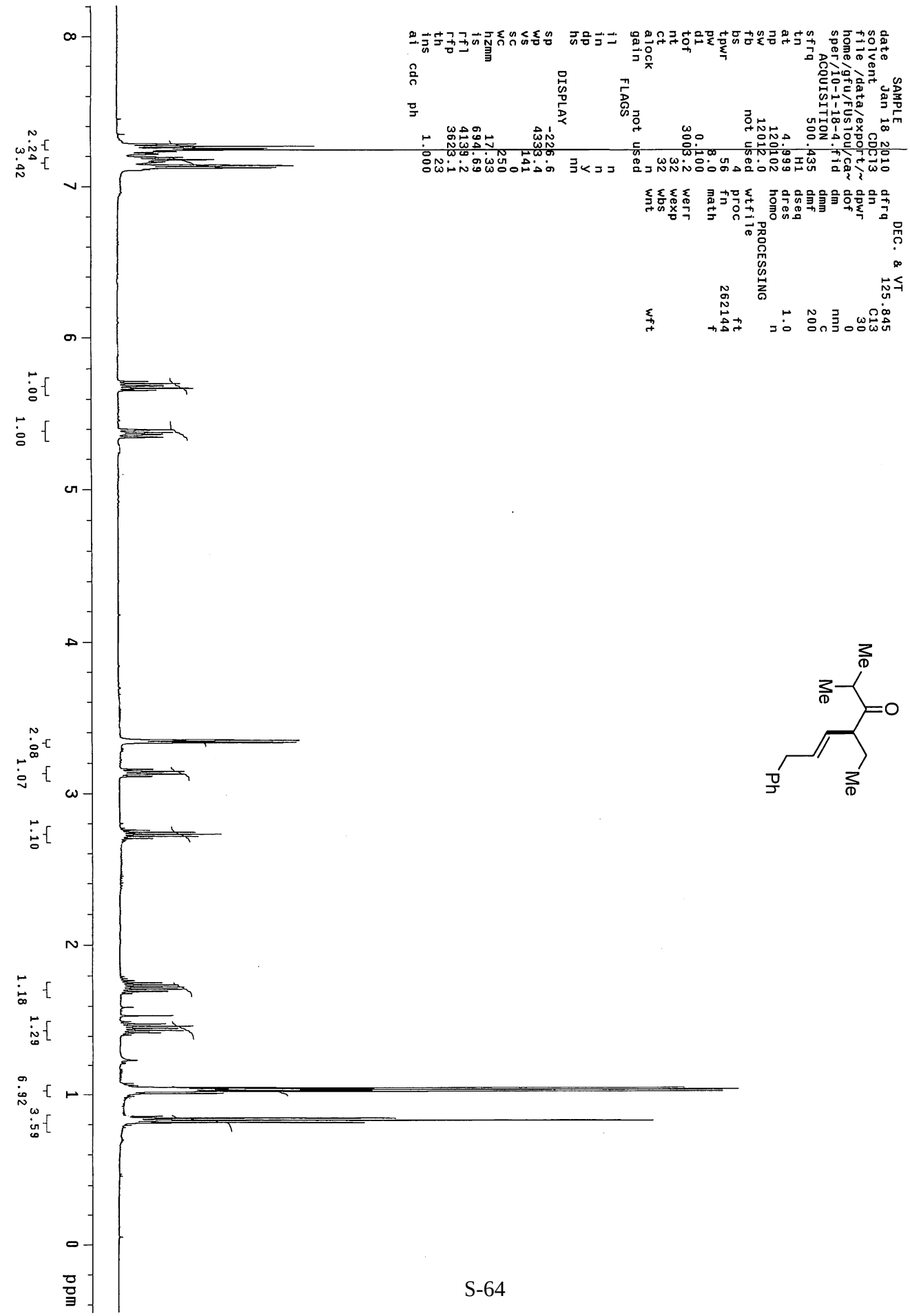


Table 3, entry 4

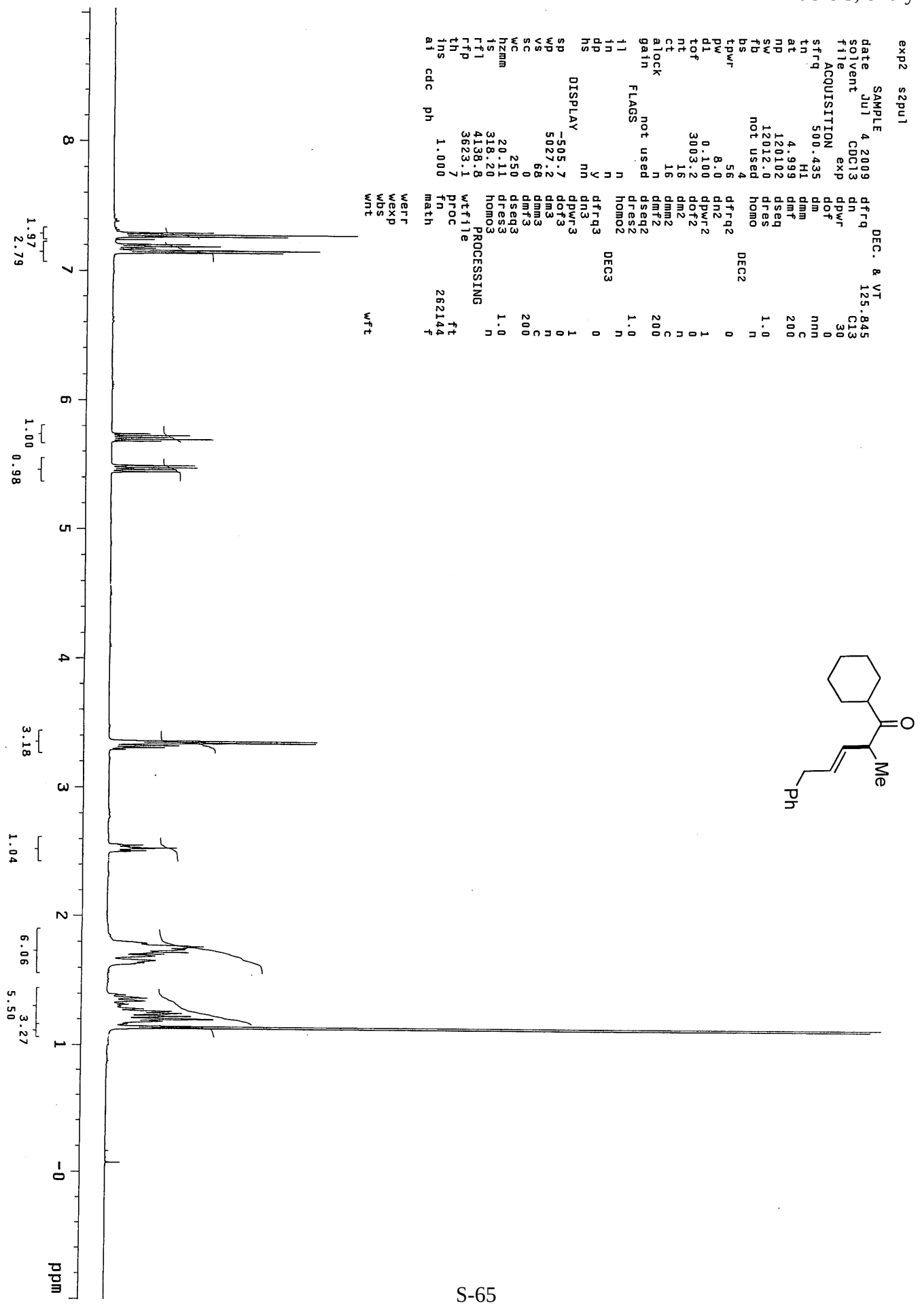
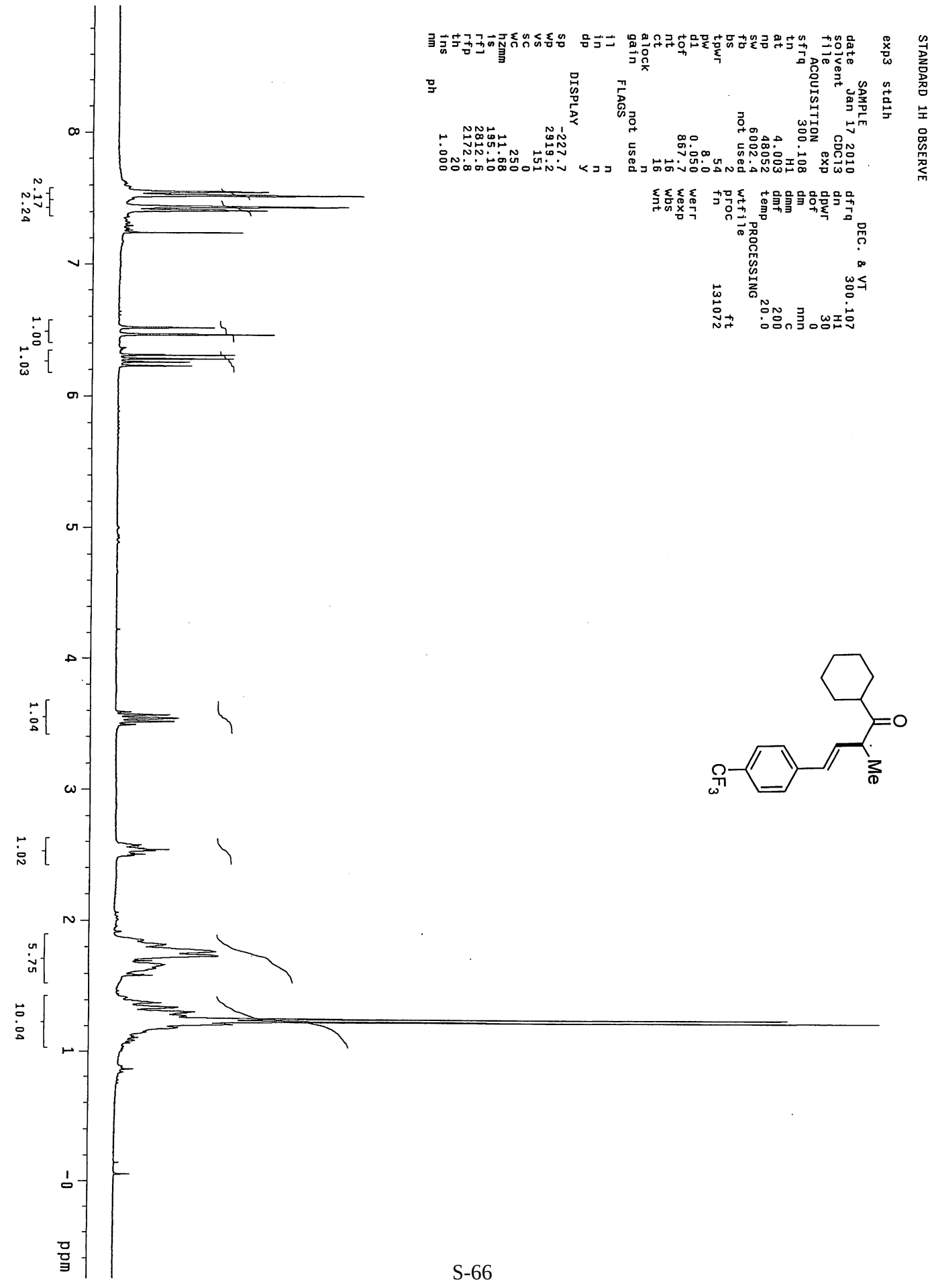
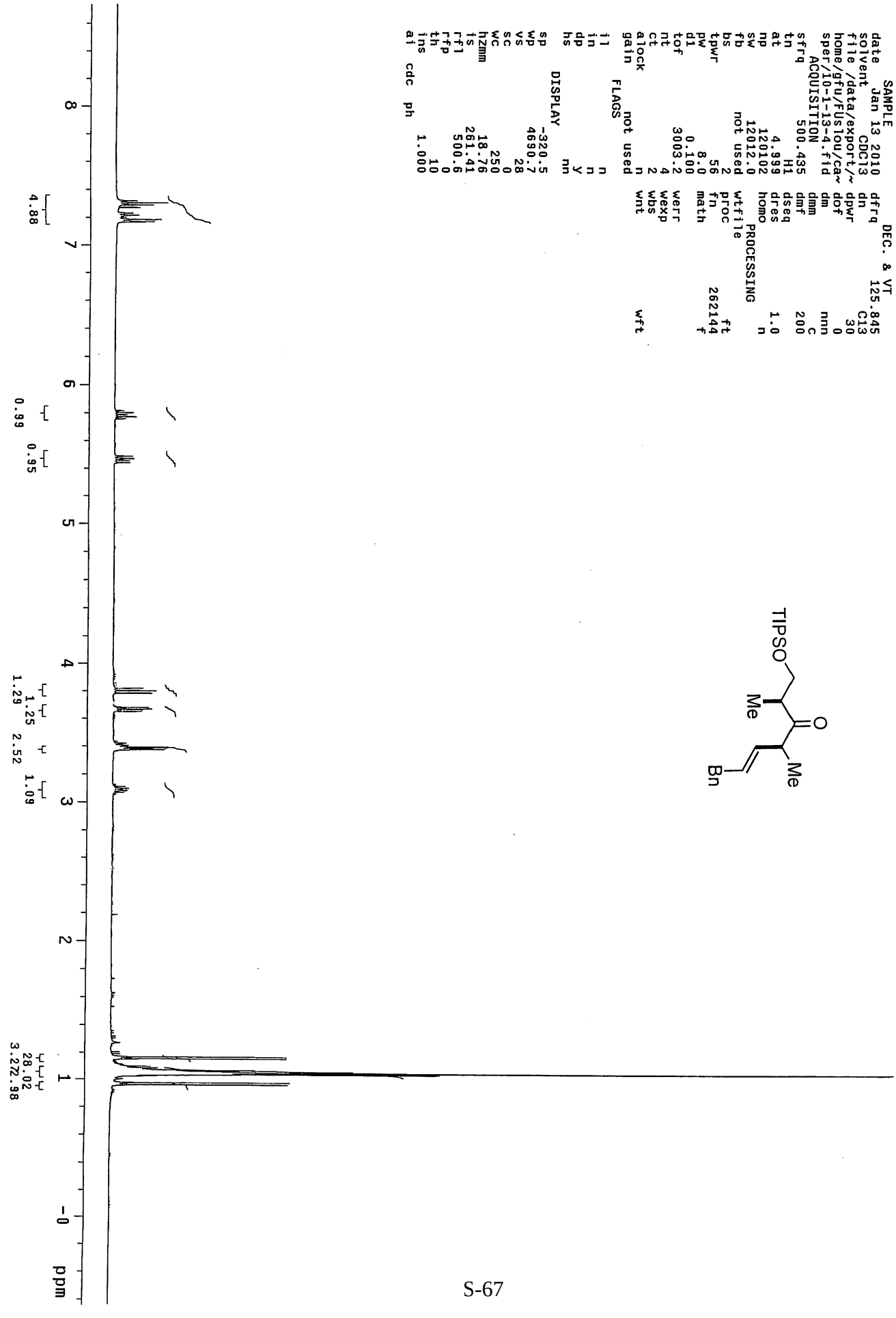


Table 3, entry 5



eq 2 product


10-1-13-4
exp1 s2pul
SAMPLE
date Jan 13 2010
solvent CDCl3
file /data/export/~
home/gfu/FUslou/ca~
sper/10-1-13-4.fid
ACQUISITION
sfrq 500.435
tn H1
at 4.999
np 120102
sw 12012.0
fb not used
bs 2
tpwr 56
pw 8.0
d1 0.100
tof 3003.2
nt 4
ct 2
alock n
gain wft
FLAGS
not used
il n
in n
dp y
hs nn
DISPLAY
sp -320.5
wp 4690.7
vs 28
sc 0
wc 250
hzmm 18.76
is 261.41
rfl 500.6
rfp 0
th 10
ins 1.000
ai cdc ph
DEC. & VT
dfrq 125.845
dn C13
dpwr 30
dof 0
nnn
dm c
dmm 200
dmf
dseq
dres 1.0
homo n
PROCESSING
wtfile
proc ft
fn 262144
math f
wexp
wbs
wnt wft
TIPSO
Me
O
Me
Bn
4.88
0.99
0.95
1.29
1.25
2.52
1.09
28.02
3.27.98
8
7
6
5
4
3
2
1
-0
ppm

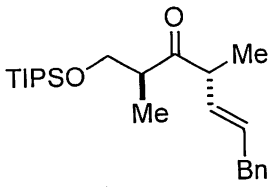
eq 3 product

10-1-20-1

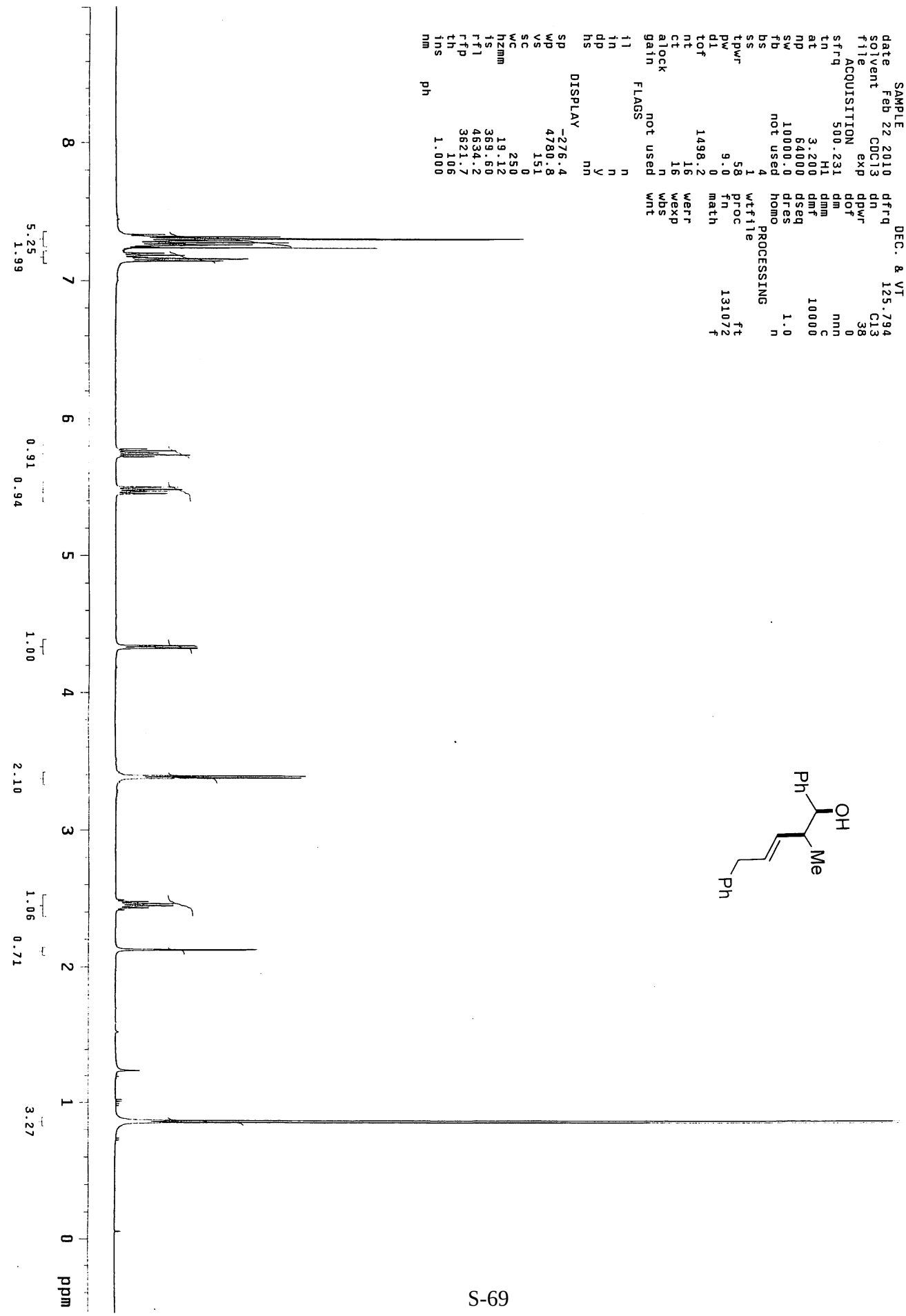
exp1 s2pul

SAMPLE		DEC. & VT	
date	Jan 20 2010	dfrq	125.845
solvent	CDCl3	dn	C13
file	/data/export/~	dpwr	30
home/gfu/FUslou/ca~		dof	0
sper/10-1-20-1.fid		dm	nnn
ACQUISITION		dmm	c
sfrq	500.435	dmf	200
tn	H1	dseq	
at	4.999	dres	1.0
np	120102	homo	n
sw	12012.0	PROCESSING	
fb	not used	wtfile	
bs	4	proc	ft
tpwr	56	fn	262144
pw	8.0	math	f
d1	0.100		
tof	3003.2	werr	
nt	32	wexp	
ct	32	wbs	
alock	n	wnt	wft
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-350.8		
wp	4393.3		
vs	37		
sc	0		
wc	250		
hzmm	17.57		
is	746.85		
rfl	500.6		
rfp	0		
th	4		
ins	1.000		

ai cdc ph



eq 4 product


10-2-22-11
expl s2pul
SAMPLE
date Feb 22 2010
solvent CDCl3
file
ACQUISITION
sfrq 500.231
tn H1
at 3.200
np 64000
sw 10000.0
fb not used
bs 4
ss 1
tpwr 58
pw 9.0
d1 0
tof 1498.2
nt 16
ct 16
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -276.4
wp 4780.8
vs 151
sc 0
wc 250
hzmm 19.12
is 369.60
rfl 4634.2
rfp 3621.7
th 106
ins 1.000
nm ph
DEC. & VT
dfrq 125.794
dn C13
dpwr 38
dof 0
dm nnn
dmm c
dmf 10000
dseq
dres 1.0
homo n
PROCESSING
wtfile
proc ft
fn 131072
math f
wnt
werr
wexp
wbs
wnt
Ph
OH
Me
Ph
8
7
6
5
4
3
2
1
0
ppm
5.25
1.99
0.91
0.94
1.00
2.10
1.06
0.71
3.27